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DIFFUSION AND SUPERSATURATION IN GELATINE.

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I. Introduction.

THE German photographer, R. Ed. Liesegang, in the course of a research on chemical reactions in gelatine[1] discovered a phenomenon which Ostwald cites as evidence that there exists a definite limit beyond which, at a given temperature and pressure, the supersaturation of a solution cannot be carried. We have undertaken an experimental study of this subject by a method based on Liesegang's discovery.

Liesegang's experiment was as follows: a glass plate was covered with gelatine impregnated with potassium chromate. The plate was laid horizontal, and upon it a drop of silver nitrate was placed. The silver nitrate diffused slowly out into the gelatine, reacted with the potassium chromate, and formed a precipitate of silver chromate. The silver chromate, instead of growing continuously in the gelatine, as diffusion of the reacting substances went on, formed in distinct *rings* about the drop, as shown in Fig. 1. The formation of the precipitate in distinct rings is clearly a phenomenon of supersaturation. We have undertaken certain measurements of these rings in the hope of being able to obtain from them some understanding of the conditions that exist in supersaturated solutions. In particular we have set for ourselves the problem to calculate from these rings the rate of diffusion of the react-

[1] Chemische Reactionen in Gallerten. Düsseldorf, 1898.

ing substances, and to estimate the limit of supersaturation attained when the solid phase is not present — the so-called "Metastable Limit" of Ostwald.

Before proceeding to the experiments we shall give certain definitions and explanatory paragraphs from Ostwald's Lehrbuch.[1]

"Between a solid substance and its supersaturated solution an equilibrium is formed, which depends on the nature of the substances, the temperature and the pressure. If we leave out of account the

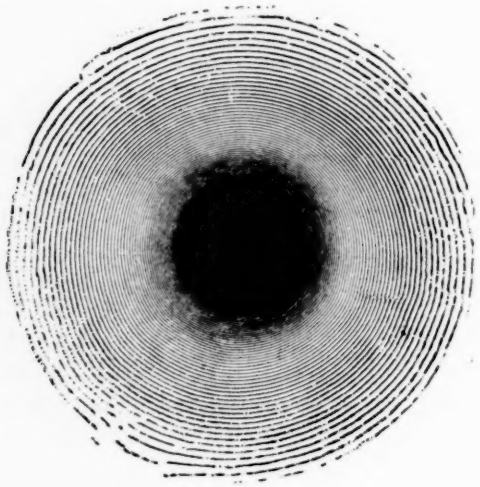


Fig. 1.

influence of the pressure, for every temperature there is a definite equilibrium. This is evidenced by a definite concentration up to which the solid substance dissolves. * * *

"When the solid phase is not present the concentration of the dissolved substance is arbitrary. The limit of concentration on one side is zero; on the other side the limit is a concentration difficult to determine, which, however, is greater than that of the equilibrium with the solid phase.

"Solutions whose concentrations exceed the concentration of saturation with a possible solid phase are called supersaturated with reference to this solid phase. * * *

"The simplest way of obtaining a supersaturated solution is to produce by change of temperature from the solid substance and

[1] Lehrbuch, II., 2, 780–784.

the solvent a solution that is more concentrated than a saturated solution at the temperature of the experiment. In most cases the temperature required to produce supersaturation is higher than the temperature of the experiment, but it can also be lower in cases where the solubility decreases with increase of temperature.

"A better way to obtain supersaturated solutions, since it is thereby easier to exclude germs of the solid phase, is to employ reactions that produce in the solvent concentrations of the substance in question in appropriate amount.

"Among supersaturated solutions there are some which under definite conditions can be kept indefinitely, if germs are excluded, without formation of the solid phase. Such solutions are called Metastable.

"On the other hand, there are some solutions in which, even when germs are excluded, the solid phase appears after a short time. Solutions of this type are called Labile.

"Metastable solutions always show smaller concentration than the labile solutions of the same substances. By increase of concentration, therefore, a metastable solution goes over into a labile condition. The concentration at which the transition occurs is called the metastable limit.

"The metastable limit is, in the first place, dependent on the nature of the substances, on the temperature, and on the pressure. In addition it is influenced by various other circumstances not yet explained. At the present time (1899) it is hardly possible to speak more definitely concerning the value of the metastable limit and the methods of determining it."

It is in connection with this discussion in the *Lehrbuch* that Ostwald cites the sharpness and regularity of Liesegang's rings as evidence that the metastable limit is something definite. But so far as we are aware, no attempt has hitherto been made to study Liesegang's rings quantitatively, and to obtain from them the actual numerical value of the metastable limit. In fact, so far as we are aware, there has not been published a determination of the metastable limit in any case. We quote further Ostwald's explanation [1] of the formation of Liesegang's ring-system:

[1] Lehrbuch, II., 2, 778.

"By the diffusion of the silver salt into gelatine containing chromate a solution is formed which is supersaturated with respect to silver chromate; precipitation does not take place until the metastable limit has been exceeded. This naturally happens simultaneously in a circle concentric with the drop. Silver chromate, in relation to which the neighborhood of the ring is supersaturated, deposits on the precipitate already formed and strengthens it; this continues until the soluble chromate has been removed from the neighborhood and deposited on the precipitate. The silver salt, diffusing on farther, supersaturates a new circular region, and the process repeats itself. Since the silver nitrate becomes more dilute by diffusion, the critical concentration at which precipitation begins is reached later and later, and the rings form farther and farther apart."

Fig. 2.

Liesegang has also shown that if the potassium chromate in gelatine is put into a capillary *tube* instead of being spread upon a plate, analogous phenomena occur when one end of the tube is dipped into a solution of silver nitrate. The precipitate in the tube is formed in layers, or discs, perpendicular to the axis of the tube (Fig. 2).

This phenomenon of the formation of a precipitate in rings on a plate or in discs in a tube is not confined to the case of a reaction between silver nitrate and potassium chromate. Liesegang found such a formation of a precipitate in the case of mercurous chromate, lead chromate and Prussian blue, in the familiar reactions which give these precipitates. We have found that with a proper choice of concentrations rings are also formed in the following cases:

TABLE I.

Diffusing Subs.	Subs. in Gel.	Precip.	Nature of Rings.
$Pb(NO_3)_2$	Na_2SO_4	$PbSO_4$	Fine. White. Close together.
$AgNO_3$	$K_2C_2O_4$	$Ag_2C_2O_4$	" " " "
"	Na_2CO_3	Ag_2CO_3	Thick. Far apart.
"	Na_2HPO_4	$Ag_4P_2O_7$	Fine. White.
"	NH_4CNS	AgCNS	" "
"	KBr	AgBr	" "
$Co(NO_3)_2$	NaOH	$Co(OH)_2$	Gelatinous. Thick.
$BaCl_2$	$K_2C_2O_4$	BaC_2O_4	Distinctly crystalline.
$HgNO_3$	KBr	HgBr	Fine. White
$FeCl_3$	Na_2CO_3	CO_2	Gas bubbles.

It is our intention to give a more extended description of the various reactions in this table at some future time. At present, however, in order to discuss the quantitative aspect of the problem, we shall confine our attention to a single case — the formation of supersaturation rings of silver chromate.

The experiment was as follows: A capillary tube of diameter .5 to 1 mm. was filled with a 1/75 or a 1/150 normal solution of potassium chromate in gelatine. After the gelatine had set, a piece of the tube about 5 cm. long, obtained by breaking the tube under water so as to expose a fresh moist surface of the gelatine, was plunged vertically into a water solution of 2N, N or N/2 $AgNO_3$ contained in a flat-walled glass vessel. By means of a cathetometer carrying a microscope of low power we watched the formation of the precipitate. After a certain period of time, depending on the concentration of the solution, the precipitate near the advancing front of the diffusing substance began to appear in layers, or discs, widely separated in comparison with their thickness. These discs appeared suddenly as sharp thin films, so that the *time* of their appearance could be determined with accuracy. The *distance* of each disc from the bottom of the tube was read off on the cathetometer. Measurements so obtained are recorded in the appended Tables IV. to XXIV. The experiment was conducted in a constant-temperature room, which, except for the short time necessary for the taking of readings, was kept dark or dimly lighted to exclude the possible action of light in hardening the gelatine.

The reaction is in accordance with the formula:

$$2AgNO_3 + K_2CrO_4 \rightleftarrows Ag_2CrO_4 + 2KNO_3$$

The advance of the reaction in the one sense or the other is conditioned upon the concentration of the active substances. For equilibrium the concentrations must satisfy the quantitative relation:

$$\overset{+}{Ag}^2 \times \overset{-}{Cr}\overset{-}{O}_4 = K \cdot Ag_2CrO_4, \qquad (a)$$

where $\overset{+}{Ag}$ and $\overset{-}{Cr}\overset{-}{O}_4$ are the concentrations of the silver ion and the chromate ion respectively, Ag_2CrO_4 the concentration of the undissociated silver chromate in solution, and K the equilibrium con-

stant. When the solid phase is present the undissociated silver chromate in solution must be in equilibrium with the solid phase, and must, therefore, be present in constant amount. In saturated solution, therefore,

$$\overset{+}{Ag}^2 \times \overset{=}{CrO}_4 = k, \qquad (1)$$

where k is the *solubility product.*

Now in supersaturated solution the mass law (Eq. *a*) is probably still true, and the question arises: Is there a relation similar to (1), with, however, a different constant product that defines the limit of supersaturation?

Is there a formula of the form

$$\overset{+}{Ag}^2 \times \overset{=}{CrO}_4 = H \qquad (2)$$

for the condition that the concentrations must satisfy when the precipitate just begins to form in the *absence* of the solid phase?

II. THEORETICAL CONSIDERATIONS.

We can calculate the value of H in equation (2) provided we can calculate the values of the concentrations of the two ions at the point and at the time at which a ring begins to appear. We propose to attempt to obtain the values of these concentrations by the mathematical theory of diffusion. To avoid possible confusion from the use of general terms we shall take the specific case in which silver chromate is the precipitated substance; the same analysis will, of course, apply to any other case.

Suppose a capillary tube (Fig. 3), containing, in gelatine, a dilute solution of potassium chromate, to be plunged at the time $t = 0$ into a vessel containing a strong solution of silver nitrate; let the distance x be measured from the end of the tube, with its positive direction along the axis of the tube; let u be the concentration of the $\overset{+}{Ag}$ ion at the point x at the time t, v the corresponding value for the $\overset{=}{CrO}_4$ ion. At the instant the tube is plunged in, that is, at the time $t = 0$, u is equal to U_0 for all negative values of x, and 0 for all positive values of x. Let 0 and V_0 be the corresponding initial values of v.

As a first approximation we may assume that the dissociation of the K_2CrO_4 is complete, since this substance is present in very dilute solution for values of x and t such as we shall need to consider; the concentration of the silver salt in the tube will also be small and we shall at present consider it to be completely dissociated. Later we can see how to correct the error introduced by

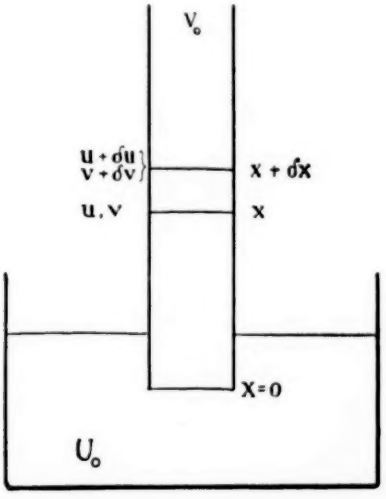


Fig. 3.

this assumption. Thus if we measure concentrations in gram-molecules, the concentration of the $\overset{+}{Ag}$ ion is the same as that of the $AgNO_3$, and the concentration of the $\overline{CrO}_4$ ion is that of the K_2CrO_4. We are to calculate the two concentrations from the diffusion of $AgNO_3$ and K_2CrO_4.

The diffusion constant is defined as the number of units of mass that will go through a unit cross-section in a unit of time under head of unit gradient of concentration. Let a^2 (essentially positive) be the diffusion constant of silver nitrate; then the quantity of silver nitrate that will cross a section S of the tube at a distance x from the origin in a time δt is the diffusion constant × gradient × time × area of cross-section. Therefore,

$$Q = -a^2 \frac{\partial u}{\partial x} \cdot \delta t \cdot S. \qquad (3)$$

The quantity crossing a section at a distance $x + \delta x$ is

$$Q + \frac{\partial Q}{\partial x} \cdot \delta x = - a^2 \frac{\partial u}{\partial x} \delta t \cdot S - a^2 \frac{\partial^2 u}{\partial x^2} \cdot \delta t \cdot \delta x \cdot S. \qquad (4)$$

The accumulation of silver nitrate in the region between x and $x + \delta x$ is the difference of these quantities,

$$a^2 \frac{\partial^2 u}{\partial x^2} \delta t \cdot \delta x \cdot S.$$

This accumulation may also be expressed as change of concentration multiplied by the volume $= \delta u \cdot \delta x \cdot S$;

$$\therefore \quad a^2 \frac{\partial^2 u}{\partial x^2} \delta t \cdot \delta x \cdot S = \delta u \cdot \delta x \cdot S,$$

whence, dividing by $\delta t \cdot \delta x \cdot S$

$$a^2 \frac{\partial^2 u}{\partial x^2} = \frac{\partial u}{\partial t} \qquad (5)$$

This is Fick's Law.[1]

Analogous considerations give us an exactly similar equation for the concentration of the $\bar{C}r\bar{O}_4$ ion at the point x and time t; namely,

$$b^2 \frac{\partial^2 v'}{\partial x^2} = \frac{\partial v'}{\partial t} \qquad (6)$$

where b^2 is the diffusion constant for potassium chromate.

In deriving these equations we have made the assumption that the formation of earlier precipitates does not materially affect the head under which the ions accumulate for the formation of new precipitates. If we make this assumption we can solve the problem completely.

Equations (5) and (6) are exactly alike, but their solutions will be different because they have to satisfy different initial conditions in the two cases. The lower end of the tube was kept constantly, by occasional stirring, at the concentration U_0, so that equation (5) must be solved subject to the condition $u = U_0$ when $x = 0$, for all values of t, and $u = 0$ for all positive values of x at the time $t = 0$. Equation (6) has for initial values $v' = V_0'$ for all positive values and

[1] Pogg. Ann., 94, 59 (1855).

$v = 0$ for all negative values of x when $t = 0$. The theory of differential equations of this type teaches us that if we can obtain any one solution for each of these equations that satisfies its boundary conditions it is the only solution. The following are unique solutions of (5) and (6) subject to these conditions:

$$u = \frac{2U_0}{\sqrt{\pi}} \int_{\frac{x}{2a\sqrt{t}}}^{\infty} e^{-\beta^2} d_i\beta, \tag{7}$$

$$v = \frac{V_0}{\sqrt{\pi}} \int_{-\frac{x}{2b\sqrt{t}}}^{\infty} e^{-\beta^2} d_i\beta, \tag{8}$$

in which $_i\beta$ is merely a variable of integration. These may be seen to be solutions of (5) and (6) respectively if we differentiate them according to the rules for the differentiation of a definite integral and substitute the results in (5) and (6). Equation (7) is also seen to satisfy the initial conditions, for if $t = 0$ and x is positive the lower limit of integration becomes ∞ which is the same as the upper limit; the integral is therefore 0 and $u = 0$. If $x = 0$ the lower limit is 0 and the value of the integral is $\sqrt{\pi}/2$

$$\therefore\ u = U_0.$$

Similar reasoning shows equation (8) to satisfy initial conditions for v.

The *metastable product* H, as we have defined it on page 8 (eq. 2), should be given by the following equation:

$$H = u^2 v = \frac{4U_0^2 V_0}{\pi^{\frac{3}{2}}} \left[\int_{\frac{x}{2a\sqrt{t}}}^{\infty} e^{-\beta^2} d_i\beta \right]^2 \cdot \int_{-\frac{x}{2b\sqrt{t}}}^{\infty} e^{-\beta^2} d_i\beta. \tag{9}$$

It is our problem to ascertain whether H is a constant for several initial concentrations of U_0 and V_0.

If we knew the diffusion constants a^2 and b^2 we could expand the integrals in (7) and (8), integrate term by term for a given value of x and t, and thus obtained u and v and from them H. This would necessitate a previous independent determination of the diffusion constants, and would beside be very laborious, as the series do not begin to converge until after the sixth or seventh term. The difficulty of the series expansion might, however, be obviated by the employment of tables that have been computed for the definite integral.

We have employed a method in which a previous independent determination of the diffusion constants was not necessary. Before passing to the solution we shall call attention to an important and easy deduction from equation (9). In order for H to be a constant the lower limits of integration

$$\frac{x}{2a\sqrt{t}} \quad \text{and} \quad \frac{-x}{2b\sqrt{t}}$$

should be constant for all rings in a given tube with given initial values of U_0 and V_0, and since a and b are constants, $x/\sqrt{t}$ should be a constant. That is, for example, if we plunge a tube containing potassium chromate in gelatine into a solution of silver nitrate and observe with a cathetometer the distance from the bottom of the tube at which each thin disc of precipitate appears, and note, at the same time, the number of seconds that have elapsed since plunging in the tube, the distance divided by the square root of the time is a constant for all the discs in this tube, and for all tubes with the same initial concentrations of the reacting substances. The following sample set of results, Table II., and all the Tables IV. to XXIV., pages 147–150, show with what consistency this conclusion is verified.

TABLE II.

Temp. 15.7. *Silver Nitrate N. Potassium Chromate N*/75.

t sec.	x cm.	$x/\sqrt{t}$.	t sec.	x cm.	$x/\sqrt{t}$.
1245	.537	.01522	3823	.940	.01520
1420	.575	.01526	4305	.998	.01521
1607	.611	.01524	4842	1.056	.01518
1825	.649	.01519	5443	1.125	.01524
2068	.694	.01526	6102	1.188	.01520
2345	.738	.01524	6870	1.260	.01520
2658	.785	.01523			.01523
3000	.834	.01523		Mean Error,	.00002
3395	.888	.01524			

III. DETERMINATION OF THE DIFFUSION CONSTANT AND THE METASTABLE LIMIT.

This constancy of $x/\sqrt{t}$ for any one set of observations under given conditions does not show, when taken alone, that there is a constant metastable solubility product H, but does show that, for a

given concentration of one of the ions, there is a definite concentration of the other ion that will cause precipitation.

In order to examine into the consistency of H, the product of ionic concentrations as defined by equation (9), we shall need to employ the data furnished by different initial concentrations of the reacting substances, as collected in the adjacent table (III.).

TABLE III.

Recapitulation from Tables IV.–XXIV. Silver nitrate 2N diffusing into

(*a*) *Potassium Chromate N*/75.

Table.	Temp.	$x/\sqrt{t}$.
IV.	16.0	.01656
V.	16.3	.01663
VI.	16.3	.01671
VII.	16.1	.01700
Mean,		.01670

Silver Nitrate N diffusing into

(*b*) *Potassium Chromate N*/75.

Table.	Temp.	$x/\sqrt{t}$.
II.	15.7	.01523
VIII.	15.5	.01524
IX.	17.0	.01549
X.	16.7	.01533
Mean,		.01530

(*d*) *Potassium Chromate N*/150.

Table.	Temp.	$x/\sqrt{t}$.
XI.	17.3	.01462
XII.	16.3	.01466
XIII.	16.7	.01467
XIV.	16.5	.01462
XV.	15.5	.01453
XVI.	16.6	.01477
XVII.	16.6	.01468
Mean,		.01465

Silver Nitrate N/2 *diffusing into*

(*c*) *Potassium Chromate N*/75.

Table.	Temp.	$x/\sqrt{t}$.
XVIII.	16.6	.01384
XIX.	16.8	.01377
	Mean,	.01380

(*e*) *Potassium Chromate N*/150.

Table.	Temp.	$x/\sqrt{t}$.
XX.	17.7	.01311
XXI.	16.9	.01292
XXII.	16.0	.01335
XXIII.	15.5	.01313
XXIV.	15.5	.01299
Mean,		.01310

Every two sets of initial concentrations, together with the corresponding values of $x/\sqrt{t}$, will give the data for calculating the

diffusion constant a^2 and the value of H, as defined by equation (9). For example, if we substitute for U_0, V_0 and $x/\sqrt{t}$ the respective values of these quantities in sections (a) and (b) of Table III., we obtain the following equations:

$$H = \frac{4 \cdot 2^2 \cdot \frac{1}{75}}{\pi^{\frac{3}{2}}} \left[\int_{\frac{.0167}{2a}}^{\infty} e^{-\beta^2} d_i \beta \right]^2 \cdot \int_{-\frac{.0167}{2b}}^{\infty} e^{-\beta^2} d_i \beta \qquad (10)$$

$$H = \frac{4 \cdot 1^2 \cdot \frac{1}{75}}{\pi^{\frac{3}{2}}} \left[\int_{\frac{.0153}{2a}}^{\infty} e^{-\beta^2} d_i \beta \right]^2 \cdot \int_{-\frac{.0153}{2b}}^{\infty} e^{-\beta^2} d_i \beta. \qquad (11)$$

These two equations must be solved as simultaneous. We have been able to do this by the aid of a set of definite integrals given in the appendix of Kramp's *Analyse des Réfractions Astronomiques et Terrestres*, published at Strassburg in 1799. Kramp's table contains values of the integral

$$\int_{a}^{\infty} e^{-\beta^2} d_i \beta$$

for 301 values of a from 0 to 3.00. This table shows, in the first place, that various values of

$$\int_{-\frac{x}{2b\sqrt{t}}}^{\infty} e^{-\beta^2} d_i \beta$$

obtained on the assumption that b^2 is of the order of magnitude of the diffusion constant of an electrolyte and that $x/\sqrt{t}$ is of the order of magnitude given by our experimental data, differ from each other and from $\sqrt{\pi}$ by less than 2 per cent. This means merely that the change of concentration, v, of the substance originally in the gelatine can be neglected.

Dividing equation (11) by equation (10) and extracting the square root we have:

$$\frac{\int_{\frac{.0153}{2a}}^{\infty} e^{-\beta^2} d_i \beta}{\int_{\frac{.0167}{2a}}^{\infty} e^{-\beta^2} d_i \beta} = 2. \qquad (12)$$

To solve this equation for a it is only necessary to find two values in Kramp's table for which the lower limits of integration are in the

ratio 0.0167 to 0.0153 and for which the value of the integral corresponding to the second is double the value of the integral corresponding to the first.

To give an idea of the procedure in such a calculation we shall give a few values from Kramp's table in the neighborhood of the solution, of which the starred value is seen to be the one satisfying equation (12).

The ratio of 0.0167 to 0.0153 is 1.091.

α and α_1 are the lower limits of integration, A and A_1 the corresponding values of the integral. The correct solution is singled out by the relation $A/A_1 = 2$.

α	α_1	α_1/α	A	A_1	A/A_1
1.77	1.932	1.091	.010909	.005677	1.921
1.79	1.954	"	.010067	.005077	1.983
* 1.80	1.965	"	.009668	.004837	1.999
1.81	1.975	"	.009284	.004632	2.005
1.83	1.999	"	.008555	.004164	2.055

From which the value of α that most nearly satisfies equation (12) is seen to be 1.80.

$$\therefore \quad \frac{.0153}{2a} = 1.80,$$

$$a = 4.25 \times 10^{-3}.$$

The corresponding value A of the integral is .009668. Therefore from equation (11)

$$H = \frac{4}{75\pi}(.009668)^2$$

$$= 1.6 \times 10^{-6}\left(\frac{\text{gm. mol.}}{\text{liter}}\right)^3.$$

The diffusion constant is not a, but a^2, which reduced to the usual units with the day as unit of time by multiplying a^2 by 8.64×10^4 becomes

$$a^2 = 1.56 \text{ (cm}^2\text{/day)}.$$

In this calculation of H the reacting substances have been assumed to be completely dissociated. The result of the calculation shows

that the concentration of the silver ion was about 1/200 normal and that of the chromate ion 1/75 normal when precipitation occurred. The dissociation of $N/200$ silver nitrate differs so little from that of $N/400$ which enters into the calculation of subsequent cases that the assumption of its complete dissociation introduces no appreciable inaccuracy. On the other hand the dissociation of $N/150$ potassium chromate is about 1.05 times the dissociation of $N/75$, and this factor representing the ratio of dissociation must be introduced into calculations involving different concentrations of potassium chromate in the gelatine.

Observing this precaution we obtain the following values for a^2 and H from other sets of data of Table III.

RESULTS.

For the Diffusion Constant of Silver Nitrate and the Metastable Solubility Product of Silver Chromate in Gelatine at 16° C.

From Table III. Data.	Diffusion Constant. cm²/Day.	Metastable Product. $\left(\frac{\text{G. Mol}}{\text{Liter}}\right)^3$
(*a*) and (*b*)	1.56	1.6×10^{-6}
(*b*) and (*c*)	1.56	1.6×10^{-6}
(*a*) and (*c*)	1.56	1.4×10^{-6}
(*d*) and (*e*)	1.53	1.3×10^{-6}
(*b*) and (*d*)	1.50	1.1×10^{-6}
(*c*) and (*e*)	1.53	1.3×10^{-6}
Mean.	1.54	1.4×10^{-6}

IV. DISCUSSION OF RESULTS.

The values obtained for the diffusion constant and for the metastable solubility product are constant within the limit of error of the method, as will be seen by a reference to the recapitulation of Table III. While the value of $x/\sqrt{t}$ for any particular tube is constant within one or two tenths of one per cent. the same good agreement is not obtained when several series of observations are made upon different tubes under as nearly as possible the same conditions. The mean deviation of different tubes from the average is as great as one per cent. We think this deviation can be accounted for by lack of uniformity in the bore of some of the tubes, so that the diffusion takes place in a conical cavity instead

of in a truly cylindrical cavity as the theory requires. That an error of one per cent. in the determination of $x/\sqrt{t}$ will account for the variations in the values of a^2 and H may be seen by a glance at the result of a recalculation of these quantities from the data (d) and (e) of Table III., on the assumption that the correct value of $x/\sqrt{t}$ in (e) is .0130 instead of .0131; a^2 comes out to be 1.63 cm.^{2}/ day and H becomes 1.9×10^{-6}. Or assuming $x/\sqrt{t}$ to be .0132 instead of .0131, a^2 becomes 1.42 and H becomes 0.7×10^{-6}.

In view of this sensitive dependence of the diffusion constant and the metastable product on the value of $x/\sqrt{t}$, we consider the results to be satisfactorily consistent.

We have not been able to find elsewhere any determination of the value of the diffusion constant of silver nitrate in gelatine. F. Voigtlaender [1] has found that the diffusion constants of salts in agar from his own measurements are in some cases smaller, in others equal to or larger than the corresponding constants for water solutions, the solutions employed having varying concentrations. He says that the question whether the diffusion in agar and water is identical can only be answered by further observations on pure water and other gelatinous solvents, such as water glass. Voigtlaender's measurements point to the conclusion, however, that the diffusion in agar and that in water are not very different, which makes our result for silver nitrate, 1.54, seem rather high, as the values obtained by Kawalki [2] would be for silver nitrate at 16° C. 1.13 to 1.20. Calculation of the diffusion constant for silver nitrate by Nernst's formula

$$a^2 = 0.0477 \times 10^7 \frac{uv}{u+v}[1 + .0034(t^\circ - 18)]$$

gives the value 1.29.

It should be noted that the value we have obtained is for diffusion through gelatine containing a rather heavy solid precipitate of silver chromate, and should not, therefore, be expected to agree with diffusion in water or pure gelatine. The important fact for this discussion is that a^2 is a constant and that there is hence no incon-

[1] Zeit. Phys. Chem., 3, p. 317, 1889.
[2] W. A., 52, p. 300, 1894.

sistency in the conclusion that the metastable solubility product of silver chromate in gelatine is a definite constant quantity satisfying the relation

$$H = \dot{Ag}^2 \times \bar{C}r\bar{O}_4.$$

As to the value of H, there are no other determinations of this quantity with which we might compare our results. As far as we know there have not been published any numerical data as to the value of the metastable product in any case. The ordinary solubility product of silver chromate in saturated water solution in the presence of the solid phase is 5.1×10^{-13} as determined by Kohlrausch.[1] The concentrations of Ag_2CrO_4 in the two cases are in the ratio $\sqrt[3]{1.4 \times 10^{-6}}/\sqrt[3]{5.1 \times 10^{-13}}$. This means that the supersaturated gelatine at the concentration of precipitation held in solution 145 times the amount of silver chromate required to saturate it in the presence of the solid phase.

Lobry de Bruyn[2] and Liesegang[3] have shown that in the case of a large number of substances, which, like the silver haloids, form amorphous precipitates, gelatine inhibits precipitation. This phenomenon is especially easy to observe and demonstrate in the case of colored substances like silver chromate and lead iodide. It is well known that electrolytes whether or not they act chemically on the colloid may cause the precipitation of a colloid from solution, and it might be supposed that the case we are discussing can be explained as such an action of the diffusing silver nitrate in throwing down colloidal silver chromate. We are of the opinion that this is not the case, because, first, precipitation is here sudden and not slow, as is the case when colloids are precipitated by electrolytes, and second, in the several cases of different concentrations of the reacting substances, the precipitate is formed, not for a constant concentration of the diffusing electrolyte, but for a constant value of the product

$$\dot{Ag}^2 \times \dot{Cr}\bar{O}_4.$$

Purification of the Gelatine. — The best commercial gelatine contains usually about 2 per cent. of ash consisting of phosphates and

[1] Leitver. d. Elektrolyten, p. 202.
[2] Rec. trav. chim. Pays-bas., 19, p. 236.
[3] Phot. Wochenblatt, 1894, p. 229.

carbonates, both of which form insoluble compounds with silver. Although the silver salts of these radicals are more soluble than silver chromate it was thought necessary to remove them and other salts as thoroughly as possible from the gelatine to avoid their possible influence on the precipitation of the silver chromate. This removal was effected by electrolyzing the gelatine between membranes of parchment paper at 500 volts continually for a week, during which time the membranes and electrodes were frequently washed by a stream of distilled water. Specimens of gelatine so prepared gave but a trace of ash on ignition.

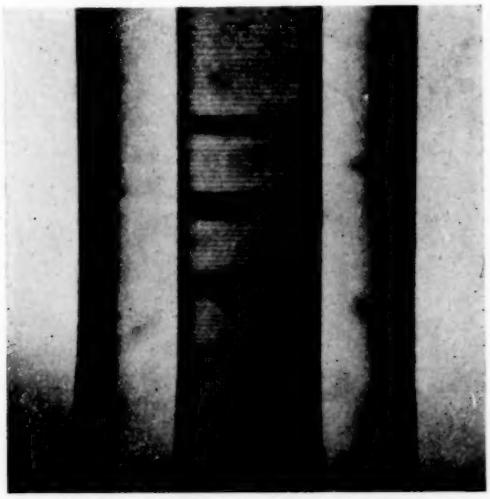


Fig. 4. Precipitation in commercial gelatine showing fine white lines between the heavy dark deposits of Ag_2CrO_4. This is a section of a tube like Fig. 2, magnified 10 diameters.

Liesegang in his original research on reactions in gelatine solutions in capillary tubes found two classes of rings; the heavy widely separated red deposits of silver chromate, and beyond these and between them another series consisting of fine, microscopic white lines. According to Liesegang's description when the time came for the formation of a new red line one of the fine white lines suddenly became yellow and grew broader until it encompassed four of the white lines and developed into the dark red of silver chromate. Liesegang observed, however, that these white lines are not

necessary for the formation of the red ones and are not present when chromate diffuses into gelatine impregnated with silver. We are of the opinion that these secondary white lines are due to the presence of impurities in the gelatine, since they appear with the same distinctness when silver nitrate diffuses into commercial gelatine to which nothing has been added. They did not appear in our purest electrolyzed gelatine. The addition of soluble chlorides, bromides or iodides in very small quantities causes the white rings to appear. Figs. 4 and 5 shows them between the larger lines of silver chromate. It is our intention to investigate further the possible influence of impurities on the formation of these precipitates.

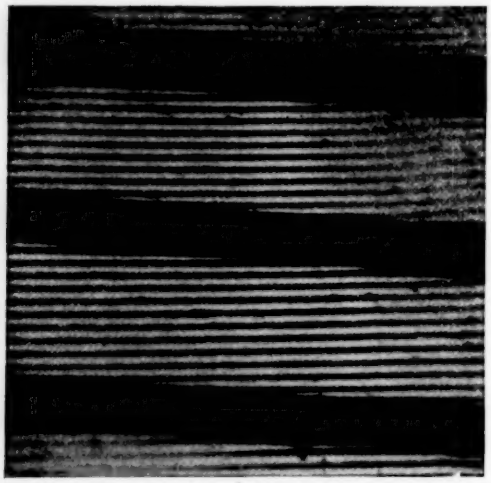


Fig. 5. Section of a plate like Fig. 1, magnified 20 times, showing two sets of rings in commercial gelatine.

It is of interest to know that gelatine is not necessary for the production of rings, for when a very fine capillary tube filled with a *water solution* of potassium chromate is carefully plunged into a silver nitrate solution precisely similar phenomena may be observed. In this case, however, the layer of precipitate exists for only a short time after its formation. It breaks up under the influence of gravity and convection and mingles with the mass of silver chromate below. Three or four layers may exist at the same time, those of later formation being sharp, and the older ones gradually disintegrating into a mass of precipitate.

V. Conclusion.

We have shown by quantitative measurement that there exists in the case of the formation of silver chromate in gelatine solution a definite constant product

$$\dot{Ag}^2 \times \bar{C}r\bar{O}_4 = H,$$

which determines the limit of supersaturation with respect to silver chromate in the absence of the solid phase.

Incidentally we have obtained a value for the diffusion constant of silver nitrate diffusing through gelatine containing solid silver chromate.

Table IV.

Temp. 16.0. *Silver Nitrate* 2*N*. *Potassium Chromate N*/75.

t sec.	*x* cm.	$x/\sqrt{t}$.
1732	.687	.01650
1920	.723	.01650
2350	.801	.01652
2596	.845	.01659
2865	.888	.01659
3170	.934	.01659
3505	.982	.01659
3870	1.032	.01662
4315	1.083	.01652
4900	1.139	.01662
		.01656

Table V.

Temp. 16.3. *Silver Nitrate* 2*N*. *Potassium Chromate N*/75.

t sec.	*x* cm.	$x/\sqrt{t}$.
1625	.672	.01667
1805	.705	.01660
2000	.742	.01660
2215	.782	.01662
2450	.822	.01661
2710	.866	.01663
2995	.910	.01663
3300	.955	.01663
3645	1.003	.01662
4020	1.051	.01658
4430	1.107	.01663
4885	1.162	.01663
5365	1.220	.01666
5895	1.280	.01667
		.01663

Table VI.

Temp. 16.3. *Silver Nitrate* 2*N*. *Potassium Chromate N*/75.

t sec.	*x* cm.	$x/\sqrt{t}$.
1705	.684	.01657
1885	.719	.01655
2083	.760	.01662
2300	.798	.01665
2540	.842	.01671
3090	.930	.01673
3405	.976	.01763
3740	1.023	.01673
4110	1.077	.01680
4525	1.128	.01679
		.01671

Table VII.

Temp. 16.1. *Silver Nitrate* 2*N*. *Potassium Chromate N*/75.

t sec.	*x* cm.	$x/\sqrt{t}$.
1580	.674	.01696
1750	.711	.01700
1940	.747	.01694
2150	.788	.01700
2385	.830	.01700
2625	.870	.01702
2910	.920	.01703
3215	.963	.01699
3550	1.015	.01704
3920	1.065	.01701
4320	1.117	.01700
4755	1.171	.01699
		.01700

TABLE VIII.

Temp. 15.5. *Silver Nitrate N. Potassium Chromate N/75.*

t sec.	x cm.	$x/\sqrt{t}$.
1530	.598	.01529
1745	.638	.01527
1985	.680	.01526
2564	.771	.01523
2903	.819	.01521
3290	.872	.01521
3720	.927	.01521
4210	.986	.01524
		.01524

TABLE IX.

Temp. 16.7. *Silver Nitrate N. Potassium Chromate N/75.*

t sec.	x cm.	$x/\sqrt{t}$.
1440	.585	.01535
1605	.619	.01545
1795	.655	.01546
2010	.695	.01551
2240	.734	.01551
2785	.819	.01551
3450	.911	.01551
3845	.964	.01555
		.01549

TABLE X.

Temp. 16.7. *Silver Nitrate N. Potassium Chromate N/75.*

t sec.	x cm.	$x/\sqrt{t}$.
1073	.498	.01520
1165	.523	.01532
1270	.546	.01532
1500	.594	.01534
1635	.622	.01538
1778	.649	.01538
1935	.675	.01535
2105	.706	.01539
		.01533

TABLE XI.

Temp. 17.3. *Silver Nitrate N. Potassium Chromate N/150.*

t sec.	x cm.	$x/\sqrt{t}$.
1332	.529	.01450
1535	.575	.01468
1790	.619	.01460
2090	.670	.01465
2422	.721	.01465
2830	.780	.01466
3280	.838	.01463
		.01462

TABLE XII.

Temp. 16.3. *Silver Nitrate N. Potassium Chromate N/150.*

t sec.	x cm.	$x/\sqrt{t}$.
800	.413	.01461
920	.443	.01461
1050	.473	.01459
1215	.508	.01456
1400	.548	.01465
1605	.586	.01463
1850	.631	.01466
2120	.675	.01466
2425	.724	.01470
2780	.775	.01470
3180	.830	.01471
3633	.884	.01466
4130	.949	.01475
4710	1.013	.01474
		.01466

TABLE XIII.

Temp. 16.7. *Silver Nitrate N. Potassium Chromate N*/150.

t sec.	*x* cm.	$x/\sqrt{t}$.
1270	.520	.01459
1465	.557	.01454
1685	.602	.01466
1935	.645	.01466
2225	.694	.01471
2555	.743	.01470
2910	.794	.01471
3345	.847	.01465
3810	.908	.01471
4340	.970	.01472
		.01467

TABLE XIV.

Temp. 16.5. *Silver Nitrate N. Potassium Chromate N*/150.

t sec.	*x* cm.	$x/\sqrt{t}$.
1225	.511	.01460
1410	.551	.01468
1653	.595	.01464
1930	.644	.01466
2243	.692	.01461
2606	.746	.01461
3028	.803	.01460
3500	.862	.01457
		.01462

TABLE XV.

Temp. 15.5. *Silver Nitrate N. Potassium Chromate N*/150.

t sec.	*x* cm.	$x/\sqrt{t}$.
965	.451	.01452
1108	.484	.01454
1295	.526	.01462
1505	.564	.01454
1745	.609	.01458
2025	.654	.01453
2345	.703	.01452
2702	.755	.01453
3115	.811	.01453
3595	.872	.01455
4165	.937	.01452
4770	1.002	.01451
5500	1.077	.01452
6380	1.155	.01448
		.01453

TABLE XVI.

Temp. 16.6. *Silver Nitrate N. Potassium Chromate N*/150.

t sec.	*x* cm.	$x/\sqrt{t}$.
945	.453	.01474
1090	.485	.01469
1260	.535	.01479
1460	.564	.01476
1685	.608	.01481
1950	.654	.01481
2250	.702	.01478
2605	.756	.01481
2995	.809	.01478
3440	.867	.01478
		.01477

TABLE XVII.

Temp. 16.6. *Silver Nitrate N. Potassium Chromate N*/150.

t sec.	*x* cm.	$x/\sqrt{t}$.
1080	.479	.01458
1245	.515	.01462
1425	.554	.01468
1630	.592	.01466
1865	.637	.01475
2130	.679	.01467
2460	.728	.01468
2790	.780	.01477
3170	.833	.01479
10050	1.467	.01463
		.01468

TABLE XVIII.

Temp. 16.6. *Silver Nitrate N*/2. *Potassium Chromate N*/75.

t sec.	*x* cm.	$x/\sqrt{t}$.
905	.421	.01399
1105	.461	.01387
1210	.485	.01394
1333	.506	.01386
1468	.530	.01384
1765	.586	.01395
1935	.606	.01378
2120	.636	.01382
2316	.661	.01374
1543	.693	.01374
2780	.726	.01377
		.01384

TABLE XIX.

Temp. 16.8. *Silver Nitrate N/2. Potassium Chromate N/75.*

t sec.	x cm.	$x/\sqrt{t}$.
1625	.555	.01377
1870	.596	.01378
2145	.640	.01382
2460	.683	.01376
2820	.734	.01382
3294	.784	.01366
3705	.839	.01379
		.01377

TABLE XX.

Temp. 17.7. *Silver Nitrate N/2. Potassium Chromate N/150.*

t sec.	x cm.	$x/\sqrt{t}$.
1026	.420	.01311
1244	.460	.01304
1510	.508	.01307
1819	.558	.01308
2181	.614	.01315
2625	.672	.01312
3185	.740	.01311
3850	.819	.01320
4700	.901	.01314
5720	.988	.01307
		.01311

TABLE XXI.

Temp. 16.9. *Silver Nitrate N/2. Potassium Chromate N/150.*

t sec.	x cm.	$x/\sqrt{t}$.
705	.346	.01274
860	.380	.01296
1048	.419	.01294
1282	.465	.01298
1535	.508	.01297
1862	.559	.01295
2250	.614	.01295
2715	.674	.01293
3250	.734	.01288
		.01292

TABLE XXII.

Temp. 16.0. *Silver Nitrate N/2. Potassium Chromate N/150.*

t sec.	x cm.	$x/\sqrt{t}$.
1305	.484	.01340
1560	.529	.01340
1880	.580	.01337
2270	.633	.01329
2730	.697	.01334
3270	.761	.01331
		.01335

TABLE XXIII.

Temp. 15.5. *Silver Nitrate N/2. Potassium Chromate N/150.*

t sec.	x cm.	$x/\sqrt{t}$.
933	.400	.01310
1120	.440	.01315
1340	.481	.01314
1590	.525	.01317
1900	.572	.01312
2265	.625	.01310
2690	.681	.01313
3190	.742	.01314
		.01313

TABLE XXIV.

Temp. 15.5. *Silver Nitrate N/2. Potassium Chromate N/150.*

t sec.	x cm.	$x/\sqrt{t}$.
900	.387	.01290
1080	.427	.01299
1300	.465	.01290
1565	.513	.01297
1875	.564	.01303
2235	.615	.01301
2670	.674	.01305
3180	.738	.01306
		.01299

JEFFERSON PHYSICAL LABORATORY, HARVARD UNIVERSITY,
CAMBRIDGE, MASS., March 1, 1903.

THE HYPOTHESES OF COLOR VISION.[1]

By Frank Allen.

TO the question "How do we see?" there are but two general replies, the eye must emit something, or something from without must enter the eye. For twenty centuries this was a debated question among philosophers who took sides with the leaders of their respective schools, and vigorously upheld their theories. A complete absence of experiment in this as in other branches of science was accompanied by an astonishingly great variety of arguments and extravagant hypotheses to support their adopted opinions. Colors were ranked among the bodies of which only the names were known. When philosophers were asked, for example, why such a body was red, they answered that it was in virtue of a quality which made it appear red.

It is far from obvious that white light is very complex in its nature; and failure to discover this resulted in the confusion of mind exhibited by writers on light and colors preceding Newton's decisive experiments.

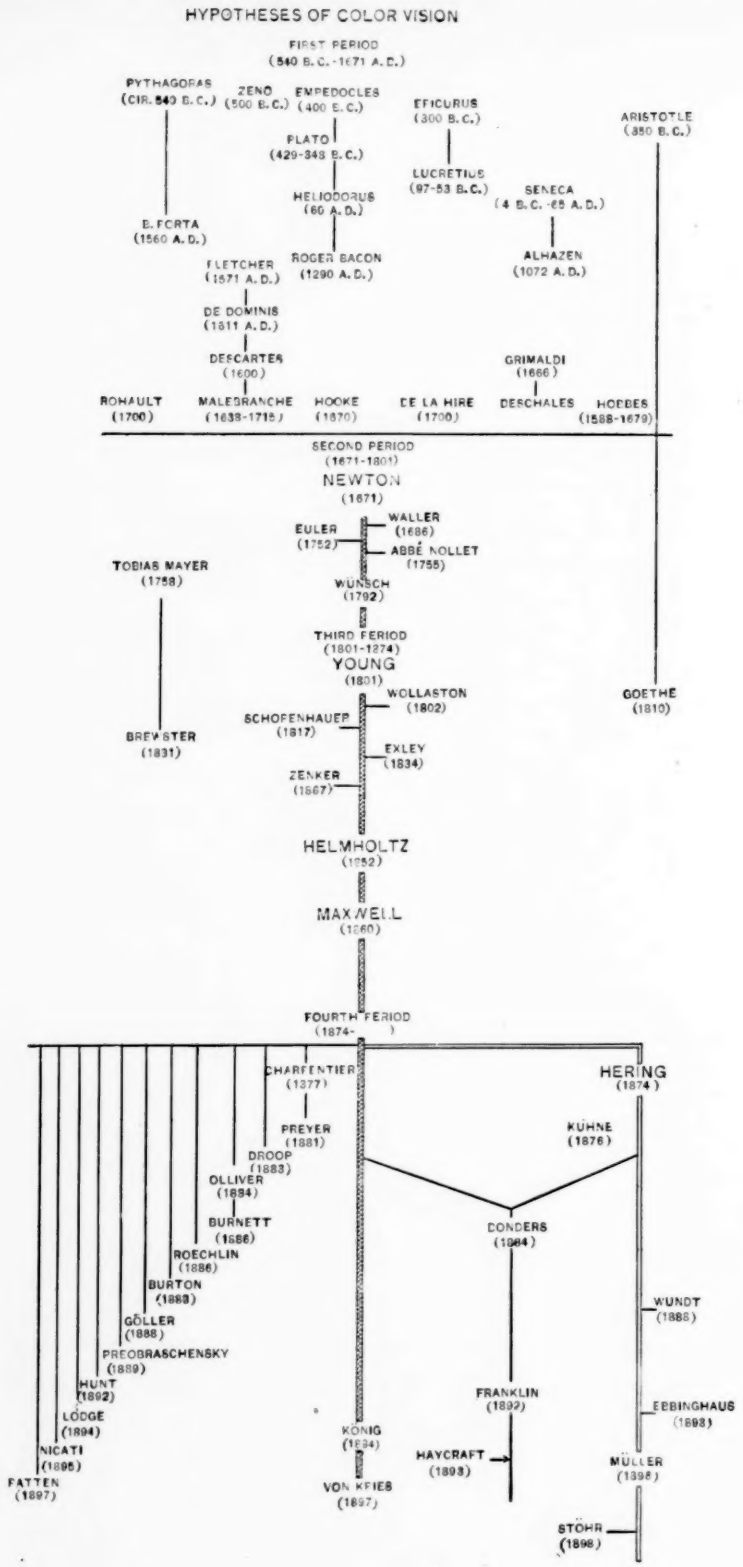
In the following short sketch of the history of this interesting branch of science an attempt is made to outline briefly most of the hypotheses of both ancient and modern writers. An outline only is attempted because a full review would expand this paper into a volume.

For the present purposes the history of color vision is here divided into four periods: first, from Pythagoras to Newton (540 B. C.–1671 A. D.); second, from Newton to Thomas Young (1671–1801); third, from Young to Ewald Hering (1801–1874); fourth, from this last date to the present time.

First Period (540 B. C.–1671 A. D.).

Pythagoras and the Pythagoreans, the second school of Grecian philosophers, who flourished about 500 B. C. held the opinion that

[1] A Report made to the Physical Seminary, Cornell University, 1902.


HYPOTHESES OF COLOR VISION
FIRST PERIOD
(540 B.C.-1671 A.D.)
PYTHAGORAS
(CIR. 540 B.C.)
ZENO
(500 B.C.)
EMPEDOCLES
(400 B.C.)
EPICURUS
(300 B.C.)
ARISTOTLE
(350 B.C.)
PLATO
(429-348 B.C.)
LUCRETIUS
(97-53 B.C.)
HELIODORUS
(60 A.D.)
SENECA
(4 B.C.-65 A.D.)
B. PORTA
(1560 A.D.)
ROGER BACON
(1290 A.D.)
ALHAZEN
(1072 A.D.)
FLETCHER
(1571 A.D.)
DE DOMINIS
(1611 A.D.)
DESCARTES
(1600)
GRIMALDI
(1666)
ROHAULT
(1700)
MALEBRANCHE
(1638-1715)
HOOKE
(1670)
DE LA HIRE
(1700)
DECHALES
HOBBES
(1588-1679)
SECOND PERIOD
(1671-1801)
NEWTON
(1671)
WALLER
(1686)
EULER
(1752)
ABBÉ NOLLET
(1758)
TOBIAS MAYER
(1758)
WUNSCH
(1792)
THIRD PERIOD
(1801-1874)
YOUNG
(1801)
WOLLASTON
(1802)
GOETHE
(1810)
SCHOPENHAUER
(1817)
BREWSTER
(1831)
EXLEY
(1834)
ZENKER
(1867)
HELMHOLTZ
(1852)
MAXWELL
(1860)
FOURTH PERIOD
(1874-)
CHARPENTIER
(1877)
HERING
(1874)
PREYER
(1881)
KÜHNE
(1876)
DROOP
(1883)
OLLIVER
(1884)
BURNETT
(1886)
CONDERS
(1884)
ROECHLIN
(1886)
BURTON
(1888)
WUNDT
(1888)
GÖLLER
(1888)
PREOBRASCHENSKY
(1889)
HUNT
(1892)
FRANKLIN
(1892)
EBBINGHAUS
(1893)
LODGE
(1894)
KÖNIG
(1894)
HAYCRAFT
(1893)
NICATI
(1895)
MÜLLER
(1896)
FATTEN
(1897)
VON KRIES
(1897)
STÖHR
(1898)

vision is caused by particles continually flying from the surfaces of bodies and entering the eye.

A century after these, Empedocles and Plato put forward the doctrine that the cause of vision is something emitted by the eye which meeting with something else that proceeds from the object is thereby reflected back again. In other words sight was considered a species of touch due to invisible feelers having their origin in the eye.

Aristotle (De Anima, Lib. 2, Cap. 6 : 350 B. C.) maintained that light is incorporeal. His ideas are best illustrated by a reference to the rainbow, in accounting for which very many theories of color production originated. He thought that the colors were due to imperfect reflection from raindrops, the image of the sun being distorted and color only exhibited. Aristotle also taught that black and white were the colors from which all others were derived, an idea which in modified form persisted to the time of Goethe. It was also supposed by some philosophers of this period that the rainbow was caused by the clouds communicating their color to the sunbeams.

Epicurus (300 B. C.) and after him Lucretius (75 B. C.) believed that we see by the intervention of light as we feel an object by means of a stick. Seneca, who flourished about 60 A. D., observed (Nat. Quest., Lib. 1, Cap. 7) that sunlight shining through an angular piece of glass gives the colors of the rainbow, which he explained as a species of false color such as is observed on the neck of a pigeon. His theory of the rainbow is interesting. "The rainbow must be circular of necessity just as waves spread in a circular manner from a disturbance in still water." Again, he says: "that the rainbow is the image of the sun reflected from a hollow moist cloud which distorts the image because of the nature and figure of the speculum. Since in water everything is seen larger, the image of the sun is large because it is reflected from a moist cloud which partakes of the nature both of glass and of water." The different colors are accounted for by supposing that they come partly from the sun, partly from the clouds, and form a mixture?

Heliodorus, a Stoic philosopher of Nero's time, adhered to the old theory of the emission of ocular beams, which he tried to strengthen by arguing from the shape of the eye.

Ptolemy, whose treatise on optics written about 150 A. D. is now lost, became the great authority on the subject to the time of Alhazen.

During the Dark Ages the Arabians were the scientific investigators. The treatises of two of them, Al Farabi and Ebu Haithem (about 1000 A. D.), are not now extant; but that of Alhazen, published about 1072, became the authority for the five succeeding centuries. His speculations on color do not however show any advance over those of European philosophers. He defines the colors of the rainbow to be three, but with Seneca supposes them to be produced by a mixture of sun's light with the blackness of the cloud from which it is reflected. In the same manner the colors of all bodies seen by reflection are tinged with the colors of the reflecting surface (Optica, p. 461). The colors due to refraction in a glass globe, he says, are not the same as those of the rainbow, because they are not of the same number and are not seen in the same way — by reflection — but by direct vision in the same manner as light itself.

Roger Bacon, who died in 1294 A. D., assented to the opinion of some of the ancients and of some of his contemporaries as well, that visual rays proceed from the eye. His great reason was that everything in nature is qualified to discharge its proper functions by its own powers in the same manner as the sun and other celestial bodies. He regarded the presence of light necessary for vision (Opus Majus, p. 289).

Johannes Baptista Porta, who published his work, "Magia Naturalis," in 1560 when but fifteen years old, performed experiments with the camera obscura, invented by himself at that time, which convinced him that vision was caused by the intromission of light into the eye. Light was considered by him to be colorless but capable of having color superinduced upon it from foreign causes. He also gives an account of the generation of each color of the rainbow from a mixture of light and the denser or rarer parts of the air. Later Porta expressed the opinion that the colors of the rainbow were produced by refraction in the whole body of rain or vapor and not in the separate drops (De refractione, p. 95).

Fletcher, of Breslau (1571), tried to account for the colors of the rainbow by means of two refractions in one drop and a reflection

from a second, but as is well known, Antonio De Dominis, Bishop of Spalatro (1611) arrived at the true explanation (De radiis visus et lucis).

To account for the color he supposed that the red rays were those that had traversed the least space inside the drop and accordingly retained most of their native force, and striking the eye more vigorously gave it a stronger sensation. Similarly green and blue were produced by those rays, the force of which had been in some measure lessened in passing through a greater body of water. All the intermediate colors were composed of mixtures of these three primaries according to the hypothesis which generally prevailed at the time.

The theory of De Dominis was adopted and mathematically investigated by Descartes (1596–1650). But while sound in his investigations of the paths of the rays, he was much less happy in the way he accounted for the production of colors. "Light is neither a substance nor yet a mere property of bodies, but the motion of a subtle fluid communicated by the pressure of a luminous body. It is affected by two motions, a circular and a direct. When the circular is quicker than the direct the color is red; if the direct is quicker the color is blue; when the motions are equal the color is yellow. All the other colors are composed of these primaries." Descartes was, however, the first to state the real nature of black and white.

Malebranche (1638–1715) modified this theory of Descartes by the substitution of a medium filled with fluid vortices instead of perfectly elastic solid globules.

Following the example of other philosophers, Thomas Hobbes (1588–1679), an English writer, published a theory based upon experiments with a prism. The colored rays he considered to be due to modified light which he divided into two parts and named "first" and "second" light. The following extracts (English Works, vol. 1, p. 459; Molesworth Edition) will give an idea of his hypothesis. "Colour is light, but troubled light, namely such as is generated by perturbed motion as shall be made manifest by the red, yellow, blue and purple which are generated by the interposition of a diaphanous prism." "It is therefore evident that when

weak but first light passeth through a more resisting diaphanous body as glass, the beams which fall upon it transversely make redness: when the same first light is stronger the transparent beams make yellowness. When the second light is strong green is produced, but when weaker it generates purple.

"Whiteness is light, but light perturbed by the reflections of many beams of light coming to the eye together within a little space. Blackness is the privation of light."

Hobbes also considered that colors are formed from a mixture of white and black.

Perhaps the most extravagant opinion ever formed upon the subject of color vision was that of Dr. Hooke the contemporary and rival of Newton. Hooke reduced the primary colors from three to two. "Blue is an impression on the retina of an oblique and confused pulse of light whose weaker part precedes and whose stronger part follows; and red is a similar impression whose stronger part precedes and whose weaker follows. The fantasm of colour is caused by the sensation of the oblique or uneven pulse of light which is capable of no more varieties than two, which arise from the two sides of the oblique pulse though they be capable of infinite gradations, each of them beginning from white and ending, one of them in the deepest scarlet and the other in the deepest blue." (Priestley "On Vision, Light and Colours.")

De la Hire, who lived at this time, supposed difference in color to depend upon the degree with which the same light affects the optic nerve. For example, red blood appears blue through the veins because the light in passing through the skin loses its power and affects the nerve with less force. In common with many other writers he assigned the blue color of the sky to the sunlight reflected by the air, seen against a background of dark space.

Grimaldi (De lumine, coloribus et iride, 1666) made the discovery that when a circular beam of light passes through a prism it forms an oblong image. He did not infer the different refrangibilities of the colored rays, but looked upon it as showing that refraction produced color as well as reflection, which was the more general way according to the philosophers. Grimaldi's idea of color was that it was condensed light, red being more condensed than blue.

He concluded with Aristotle that light is no real substance ; not a substantial but an accidental quality.

Priestley (On Vision, Light and Colours, p. 240) thus sums up the theories of color production to the time of Newton :

" The Pythagoreans called colour the superficies of a body. Plato said that it was a flame issuing from them. According to Zeno it is the first configuration of matter, and Aristotle said it was that which moved bodies actually transparent. Descartes very sensibly argued that colour is a modification of light ; but he supposed that the difference of colour arises from the prevalence of the direct or rotatory motion of the particles of which it consists. Father Grimaldi, Deschales, and many others thought the differences of colour depended upon the condensation and rarefaction of light. Malebranche was of the opinion that differences in colour depend upon the quick or slow vibrations of a certain elastic medium filling the whole universe. Rohault imagined that the different colours were made by the rays of light entering the eye at different angles with respect to the optic axis ; and from the phenomena of the rainbow he pretended to calculate the precise angle that constituted each particular colour. Lastly Dr. Hooke, the rival of Newton, imagined that colour is caused by the sensation of the oblique or uneven pulse of light ; and this being capable of no more than two varieties, he concluded that there could be no more than two primary colours."

Note.— Most of the hypotheses comprising the First Period will be found in Priestley's " On Vision, Light and Colours."

Second Period (1671–1802).

1671. Newton. " New Theory of Light and Colours." Philo. Trans. (abridgment), Vol. I., p. 678. Reprinted in Pop. Sci. Monthly, Sept., 1902.

Newton performed his experiments on the decomposition of white light in 1666, but apparently did not publish the results until several years later. The following quotations from several of his papers will give his general views on color vision.

" The rays of light to speak properly are not coloured. In them is nothing else than a certain power and disposition to stir up a sensation of this or that colour."

"To the same degree of refrangibility ever belongs the same colour, and to the same colour ever belongs the same degree of refrangibility."

"To explain colours I suppose that * * * the rays of light by impinging on the stiff refracting superficies, excite vibrations in the ether * * * of various bigness; the biggest, strongest or most potent rays, the largest vibrations; and others shorter according to their bigness, strength or power; and therefore the ends of the capillimenta of the optic nerve, which pave or face the retina, being such refracting superficies, when the rays impinge upon them, they must there excite these vibrations which * * * will run along the aqueous pores or crystalline pith of the capillimenta through the optic nerve into the sensorium; and there, I suppose, affect the sense with various colours according to their bigness and mixture; the biggest with the strongest colours, reds and yellows, the least with the weakest, blues and violets; the middle with green; and a confusion of all with white * * *."

1686. Waller: Phil. Trans., vol. 3, p. 274.

In this paper Waller describes the materials from which pigments of definite colors are made. He also briefly mentions experiments in which he mixed the simple red and yellow pigments with each of the simple blues, and concludes that these mixtures of primaries give most of the medium colors, namely, green, purple, etc.

1752. Euler: Nova theoria lucis et colorum. Lettres à une Princesse d'Allemagne, 1768. Nos. 23, 27 and 28.

Euler upheld the undulatory theory and strongly opposed the doctrine of light corpuscles. But he maintained that bodies became visible because the sun's rays fell upon them, throwing their particles into motion, generating in their turn rays which, affecting our eyes, rendered the bodies visible. The blue color of the sky he explained by supposing the dust suspended in the atmosphere to generate blue rays owing to their constituent particles being thrown into vibration by the sun's light.

1755. Abbé Nollet: Leçons de Physique, Tom. 5, Sec. 3. Quoted by J. D. Forbes: Phil. Mag., S. 3, Vol. 34, p. 172, 1849.

This writer taught the Newtonian theory of light and colors, but maintained the primary qualities of orange, green and purple.

1758. Tobias Mayer: Gottingische gelehrte anzeigen, p. 147. Quoted by Helmholtz: Phil. Mag., S. 4, Vol. 4, p. 522, 1852.

The three colors, red, yellow and blue had been mixed as pigments in early times, and came to be regarded somewhat as primary colors. "Mayer was the first to give utterance to the view that the three primitive colours might correspond to three different kinds of light, red, yellow and blue, each of which furnished rays of all refrangibilities. According to this, at every point in the solar spectrum, red, yellow and blue rays are mixed together which do not differ in refrangibility and therefore cannot be separated by the prism."

1792. Chrétien Ernest Wünsch: Versuche und Beobachtungen über die Farben des Lichtes. Leipsic. Abstracted in Annals de Chimie, 64, p. 135, 1807.

Wünsch performed many experiments to prove that there were not seven primary colors as some supposed from the number of spectrum colors given by Newton, nor yet five as others believed. He was the first to select red, green and violet as primaries, a result to which he was led by his experiments on mixtures of the colored rays of the spectrum.

Third Period (1801–1874).

1801. Thomas Young: "On Theory of Light and Colours." Phil. Trans., Vol. 92, p. 12, 1802 (read in 1801). "Some Cases of the Productions of Colours." Ibid., p. 387.

In the first paper Young selected red, yellow and blue as the three simple color sensations, with no other basis than current scientific opinion. Owing to the celebrated but misconstrued observations by Wollaston of the dark lines in the solar spectrum, Young modified his theory by selecting red, green and violet as primaries, quite independently, however, of Wünsch. This theory he further confirmed by experiments, after which it remained in obscurity until Maxwell and Hemholtz brought it to the attention of scientists and made it the basis of their investigations.

Young seems to have been the first to attribute a definite physiological significance to the three primary colors, the precise hues or

wave-lengths of which he had no means of determining. His general principles were modified and made definite by the experimental researches of Helmholtz, Maxwell, König and others. These do not all agree upon the hues selected as the primary colors, and Maxwell in particular selects a blue as the third of his triad of fundamentals.

"The referring of all colours," says Helmholtz, "to the three primitive ones has, in the case of the different observers, three different senses:

"1. That the different colours were such as permitted of the formation of all others from their combinations.

"2. Or, as supposed by Mayer and Brewster, that the primitive colours correspond to three different kinds of objective light.

"3. Or, as supposed by Young, that they correspond to three primitive modes of sensation experienced by the visual nerves, and from which the remaining sensations of colour are composed."

[Helmholtz: "On the Theory of Compound Colours." Phil. Mag., S. 4, Vol. 4, 1852, p. 522. Also "Physiol. Optik."]

[Maxwell: "On Theory of Compound Colours, and the Relations of the Colours of the Spectrum." Phil. Trans., p. 57, 1860.] See also A. M. Mayer: "History of Young's Discovery of his Theory of Colors." Amer. Jour. of Science, Ser. 3, Vol. 9, p. 251, 1875.

1802. William Hyde Wollaston: "A method of examining refractive and dispersive powers by prismatic reflection." Phil. Trans., Vol. 92, p. 378.

In this paper Wollaston records his discovery of the principal "Fraunhofer" lines, the nature of which he was far from suspecting. He supposed that they divided the spectrum into four parts and formed the boundaries of the four corresponding colors, red, yellowish-green, blue and violet, the color of each division being quite uniform. He says that "we may distinguish, upon the whole, six species of rays into which a sunbeam is divisible by refraction." These are the four visible ones mentioned and in addition the invisible ultra-violet and infra-red. Wollaston evidently considered his four colors to be simple objective colored light.

This paper was important since it led Young to revise his theory.

1810. Goethe: "Farbenlehre." English translation, "Theory of Colours." Eastlake.

The hypothesis of Goethe is merely the absurd doctrine of the ancients that color is a mixture of light and darkness developed to a very high degree. "Light and darkness," Goethe says in the introduction to his work, "or light and its absence are necessary to the production of color." He bases his views on observations made by looking at a broad field of light (*e. g.*, a window) through a prism, and draws the general conclusion that next to the light a color appears which is called yellow; another appears next to the darkness which we call blue. When these are mixed in equal proportions the resulting color is green. All these colors produce new tints by being mixed with darkness.

Goethe's writings on color are remarkable for the abuse and denunciaton which he heaped upon the experiments and color theory of Newton. To some of the propositions of Newton he applied such terms as "incredibly impudent," "mere twaddle," "ludicrous explanation," and others of a similar character.

1816. Schopenhauer: "Ueber das Sehen und die Farben." Abstract in Encyc. Brit., Vol. 21, p. 450.

"The distinction of white and black with their mean point in the gray is referred to the activity or inactivity of the total retina in the graduated presence or absence of full light. The eye is endowed with polarity by which its activity is divided into two parts qualitatively distinct. It is this circumstance that gives rise to phenomena of colour. All colours are complementary. Each pair makes up the whole activity of the retina and so is equivalent to white; and the two particular activities are so connected that when the first is exhausted the other spontaneously succeeds. Such pairs are infinite in number. But there are three pairs which stand out prominently and admit of easy expression for the ratio in which each contributes to the total action. Red and green (each equal to ½); orange and blue (2 : 1); yellow and violet (3 : 1).

1831. Brewster: On a New Analysis of Solar Light. Trans. Roy. Soc. Edin., Vol. 12, p. 123, 1834. (Read in 1831.)

Awarded the Keith Biennial Prize in 1834 by Roy. Soc. of Edin.

The theory of Brewster is an elaboration of that of Mayer based on observations of an *impure* spectrum. The main points of the theory are as follows:

1. Red, yellow and blue light exist at every point of the solar spectrum.

2. As certain proportions of red, yellow and blue lights constitute white, the color of every point of the spectrum may be considered as consisting of the predominating color at any point mixed with white light.

3. By absorbing the excess of any color at any point, white light appears at that point which cannot be decomposed by any number of refractions.

The great reputation of Brewster induced most physicists for more than twenty years to adopt this view, Airy, Melloni, Draper, and Helmholtz alone dissenting. This theory persists to the present time, and as Rood remarks, is almost universally believed by artists.

Helmholtz investigated the experiments which misled Brewster, and showed that he had employed a spectrum mixed with stray white light.

1834. Thomas Exley. "Physical Optics," p. 28.

The following condensed extract will give a general idea of the views of this writer:

"The atoms of light have equal velocities, but unequal momenta and spheres of repulsion; hence they ought to produce different effects or sensations on the delicate organ of vision. Probably those ethereal atoms which penetrate deepest into the sensitive part of the eye to produce their greatest effect give the red color, and those which pierce to the least depth produce violet, and those intermediate in proportion. Therefore the atoms which have the greatest absolute force and the least sphere of repulsion will cause a red color, and others according to one or other or to the proportion of both these circumstances will produce the same or other colors."

1867. W. Zenker. "Versuch einer Theorie der Farben perception." Archiv für Mikroskopische Anatomie (Schultze), Bd. 3, p. 248.

The retinal layer from which the rods and cones project acts as light reflector, according to the author. The layer of rods and

cones is supposed to have a greater refractive index than the layer above. Part of the light entering the eye is absorbed, and part reflected, the latter being the portion of the radiant energy which excites the sensation of color. The elements of the retina may be considered as systems of surfaces upon which the incident light-waves fall perpendicularly, and from which they are reflected in the same manner. These result in systems of standing waves with nodes at fixed distances from the reflecting layer, the distances depending upon the wave-lengths. The point of maximum disturbance will therefore be different for waves of different refrangibilities. The rods and cones, he says, are like piles of plates, each plate having a thickness equal to three standing waves of red, four of blue, and five of violet. The loops of the standing red waves will therefore always affect different plates from those acted upon by blue and violet, and hence these sensations will always be excited by the proper wave-lengths. This theory accordingly makes color perception a function of space not of time.

Fourth Period (1874–).

1874. Ewald Hering. A series of six papers in: Sitzungs. der Kaiserl. Akad. der Wissen. zu Wien. (Math.-Naturwiss. Classe). Fifth paper: Grundzüge einer Theorie des Lichtsinnes. 69 (3), p. 179, 1874. Sixth paper: 70 (3), p. 169.

Papers collected under the title: Zur Lehre vom Licht-sinnes. Vienna, 1878.

The hypothesis of Hering, the great rival of the Young-Helmholtz theory, is based upon the idea of visual substances. Hering assumes six psychophysical processes corresponding to six primary sensations which may be arranged in complementary pairs, black-white, blue-yellow, green-red. Three photochemical substances are supposed to exist in the retina, one corresponding to each of the pairs of sensations. The sensations of white, yellow and red are caused by the dissimilation of the corresponding visual substances, and the sensations of black, blue and green are caused by the assimilation of the same substances. These substances are not present in equal amounts. All the rays of the visible spectrum have a dis-

similating action on the black-white substance, but different rays in different degrees. Mixed light appears colorless when it acts on the blue-yellow or red-green substance with equal dissimilative and assimilative power. The effects are not complementary merely but antagonistic. For example, fundamental red and green do not produce white by their combination, but merely destroy each other's effect and leave visible the white which is already there. This is not strictly true of the white-black antagonism, for their actions do not destroy each other but give rise to a series of grays. Each visual sensation is really a mixture of all six fundamental sensations. The one of the six which has relatively the greatest weight gives the character and name to the mixed sensation.

1876. Kühne. Papers in: "Verhandlungen des Naturhistorische-Medicinischen Vereins zu Heidelberg," 1877–79.

Following close upon the discovery (1876) by Boll of the "Visual purple," Kühne constructed a theory of vision. He supposes that the waves of light give rise in the retina to different compounds according to their length, and thus produce the different color sensations.

1877. Augustin Charpentier. "De la vision avec les diverses parties de la rétine." Archives de Physiol., 4, p. 894; also, "Sur la distinction entre les sensations luminenses et les sensations chromatiques," Compt. Rend., 86, 1878, pp. 1272 and 1341. Theory further developed in numerous other short papers in Compt. Rend., *e. g.*, 2 Semes, 1885, p. 275. Also see Nineteenth Century, August, 1893, Vol. 34, p. 258 in art. "Recent Science" by Kropotkin.

This theory distinguishes in optical phenomena: first, a luminous sensation; second, a chromatic sensation; third, a visual sensation, or a sensation of form. Charpentier supposes a double process—chemical and thermal—of colored light upon two different pigments of the retina. The photochemical effect of light decomposes the visual purple and generates in the optic nerve one sort of vibrations totally independent of the color, and varying in amplitude with the intensity. Another pigment is supposed to be located between the rods and the cones which absorbs light and heat. This absorption generates in the nerve another set of thermal or thermo-electric un-

dulations which always begin a little later than the former, the interval being greater for violet than for red.

Two waves are thus moving along the optic nerve with corresponding phases at different intervals. Their various combinations provoke a variety of sensations which we interpret as so many colors.

1881. W. Preyer: "Ueber den Farben- und Temperatursinn mit besonderer Rücksicht auf Farbenblindheit," Pflüger's Archiv, Bd. 25, p. 31.

In every color sensation Preyer distinguishes three parts: quantity or intensity; quality or tone; temperature. The intensity depends upon the force with which the retina is acted upon by the ether waves, the quality upon their amplitude. He also makes an æsthetic division of colors into two classes, warm and cold. The warm colors are from red to yellow green, the cold from this latter to violet. The color process is developed from an earlier existing temperature sense, and indeed the color sense may be considered a special case of the thermal sense limited to the retina. In this hypothesis, each retinal nerve fiber sensitive to color impressions terminates in two "cones," one of which is excited by warm colors and the other by cold, the deciding factor being the wave-length. The rods give sensations only of white, gray, and black, the cones the color sensations.

1882. E. Landolt: "Théorie de la perception des couleurs," Arch. d'Ophthalm., II., p. 79.

1883. H. R. Droop: "Colour Sensations," Phil. Mag., S. 5, 15, p. 373.

This very indefinite theory of color vision is based upon two cases of color blindness described by Holmgren. One of the persons saw only red and bluish green in the spectrum and was blind to blue and yellow; the other saw yellow and blue, but was blind to red and green. As these were cases of monocular color-blindness their observations were accurately described. From these data he outlines a theory comprising five fundamental sensations, the complementary pairs red-green, yellow-blue, and the sensation of white. No suggestion is given as to what are the retinal processes by which the colors are perceived.

1884. A. Angelucci: "Una nuova teoria sulla visione," communic. preventiva presentata All' Acad. Med. de Roma, 14 July, 1884. Also in: Rec. d'Ophthalm., p. 34, 1886.

1884. F. C. Donders: "Noch einmal die Farbensysteme," Graefe's Archiv für Ophthalmologie, Bd. 30 (1), p. 15.

The theory of Donders comprises features of both the Young-Helmholtz and Hering theories, and at the same time introduces some new ideas of the possible mechanism of color perception; the most prominent being that of successive partial dissociation of the complex color molecules of a single visual substance, which gives rise to the four simple color sensations, red, yellow, green and blue. It is thus a four-color theory, but he supplemented this by a three color theory (red, green, violet) under certain conditions in order to obtain for his theory the advantages which a three-color theory has.

1884. C. A. Olliver. "A Correlation Theory of Colour Perception." Phila. Med. Times, 14, p. 715, 1883–4.

"Each and every healthy optic-nerve filament transmits to the color-center of the brain for recognition, nerve energies equal to as many special sensations as its peripheral tip is capable of perceiving. Color perception takes place through each and every optic nerve filament." Instead of separate nerves for several independent fundamental color sensations with the retina as the distinguishing factor, the "color-center" of the brain perceives color according to the specific energy transmitted.

1886. Roechlin.

The theory of this writer is that yellow and blue are the only two simple colors of the spectrum, the third being always found fused with yellow or blue to form reds and violets. Roechlin asserts that purple may be produced by combining violet and yellow, as well as by the mixture of red and blue.

1886. S. W. Burnett. "The new Theory of Color-perception." Amer. Jour. Ophthal., Vol. 3, p. 278.

In this theory the brain is made the differentiating organ, and the nerve fiber is supposed to undergo different changes according to the different colors striking the retina. The same nerve is the conducting apparatus for different colors, which set up corresponding undulations, and these are the sources of different color sensations.

1888. W. Wundt. "Die Empfindungen des Lichtes und der Farben." Philos. Studien, 4, p. 311.

Apart from every external light stimulation and from all equivalent internal stimuli such as pressure, the retina is in a constant condition of internal stimulation. To this corresponds the sensation black, which also in part accompanies the light stimuli giving rise to the sensation gray.

By means of every external retinal stimulation two different excitation processes are set free — a chromatic and an achromatic — which follow different laws. With weak stimulation the achromatic has the greater intensity, with moderate light excitation the chromatic is more intense, while with the most intensive stimulation the achromatic is again predominant. The achromatic excitation consists in a *uniform* photochemical process which reaches its maximum in the yellow. The chromatic consists in a *polyform* photochemical process which represents a periodic function of the wave-length. Antagonistic action occurs not between the color stimuli themselves, but between the photochemical processes, and results in leaving a colorless light stimulus.

1888. Chas. V. Burton. "Experiments on Colour-perception, and on a Photo-Voltaic Theory of Vision." Cambridge Philos. Proc., Vol. 6, 1886–9, p. 308.

The author bases his theory upon experiments of Dewar and McKendrick (Edin. Philo. Trans., XXVII., 141), who have shown that there is a considerable electromotive force between the anterior portions of the eye and a transverse section of the optic nerve. It was found that the current flowing was altered in amount only when light fell upon the retina. Yellow and green rays produced the greatest effect. The converse phenomenon is well known that an electric current applied to the optic nerve produces a sensation of light.

The theory suggested is that electric currents in the nerve fibers produce the sensation of light, and, if of sufficient intensity, of color also. The light of all wave-lengths falling upon the retina affects these currents in various degrees, which produce the phenomena of color. Persistence of vision is explained by a reverse current due to a polarizing electromotive force.

1888. A. Göller. "Die Analyse der Lichtwellen durch das Auge." Dubois-Reymond's Archiv für Physiologie, I. and II., p. 139. Reviewed by C. L. Franklin: Am. Jour. Psych., Vol. 2, 1888–9, p. 155.

Göller explains the analysis by the eye of light waves into sensations of differently colored lights by rotatory polarization. "Monochromatic light, on entering the eye, passes through the transparent retina, and is reflected back from the pigment epithelium in a state of plane polarization. The outer members of the cones play the part of a plate of quartz — they shift the plane of polarization by a definite angle. A molecular motion of much slower period is then set up in the protoplasm of the inner members, and it is the sensitiveness of the nervous filament to the plane of this motion which constitutes the sensation of color. Two complementary colors are colors which have had their planes of polarization rotated, one ninety degrees more than the other, with a phase difference of a quarter wave-length, the amplitudes being the same. These conditions would be sufficient to cause their superimposed harmonic motions to produce the motion of circular polarization, and that would be indistinguishable from the motion produced by all the colors of white light acting together.

Two vibrations whose planes are at different angles would give an elliptic motion of such a kind that the direction of its major axis would give its tint, the excess of the major axis over the minor would give its saturation, and the minor axis would give the amount of white light mixed with it."

1889. Preobraschensky. "Hypothese des Farbensehens." Jour. Russ. Phys.-chem., phys. part. 21, p. 248. Abstract: Jour. de Phys., II., 9, 1890, p. 538.

In this article the author very seriously modifies the Young-Helmholtz theory. In place of three kinds of nerve elements he supposes two — one sensitive to waves from .400 μ to .600, the other to those between the wave-lengths .520 and .790. The simple sensations correspond to the extreme vibrations. The gray sensation is produced by the simultaneous impression of the same intensity of two colors equally distant from the extremes. The perception of the intensity of light is the same in both theories.

1892. C. L. Franklin. "Eine neue Theorie der Lichtempfindungen." Zeit. für Psych. und Physiol. der Sinnesorgane, 4, p. 211.

"On Theories of Light-Sensation." Mind, N. S., 2, 1893, p. 473.

"In the earliest stage of its development the visual sense consisted only in the sensation of gray, *i. e.*, the whole black-gray-white series of sensations. There is a certain kind of molecule, called the 'gray-molecule' which is composed of an outer range of atoms somewhat loosely attached to a firmer inner core, and having different periods of vibration. The light waves of the entire spectrum in some measure, and particularly those of the middle part, have the power of tearing off this outer sheath of atoms which react chemically upon the retinal nerve ends, and bring about the sensation of gray. The color molecules are developed from the gray molecules in the following manner: The atoms of the outer range segregate themselves into three different groups at right angles to each other, and having three different average velocities. Light of the fundamental color tones (red, green and blue) tears off from a large number of molecules those atom-groups whose periods are synchronous with the vibrations of the light, and those special chemical substances are set free which excite the respective color sensations. Intermediate waves set free atoms of two kinds and so give rise to mixtures of colors. Certain mixtures of light set free all three kinds of nerve-exciting substance which results in the gray sensation."

1892. Edmund Hunt: "Color Vision." Glasgow.

In a critical essay Hunt discusses several of the existing theories of color vision, and the interpretations of their experiments made by various writers. In addition he presents a theory of his own. Rejecting the various three-color and four-color theories, he maintains that there are five pure or principal colors: red, yellow, green, blue and purple. No attempt is made to describe any retinal processes by which the pure colors and their mixtures are perceived. Black and white are not considered as sensations.

1893. J. B. Haycraft: "A new Hypothesis concerning Vision." Proc. Roy Soc., 54, p. 272, 1893.

This paper briefly outlines an evolutionary theory in which color perception is a development of an earlier existing light-sense. To be concrete, the sensation of yellow has in the course of evolution been produced by pigments which stimulate the eye by the yellow, red and green spectral rays which they transmit. The red and green rays when mixed do not, however, give rise to red and green sensations, but simply intensify the yellow sensations. In a similar way combinations of other rays are treated.

1893. H. Ebbinghaus: "Theorie des Farbensehens." Zeit. für Psych. u. Physiol. der Sinnes., 5, p. 145. Reviewed by C. L. Franklin. Mind, N. S., 3, p. 198, 1894.

This theory is a development of Hering's, with the distinctive idea—partial dissociation—of Donders. "The visual purple is identical with a photochemical substance of such a nature that its primary partial dissociation is the cause of the sensation of yellow, and its completed dissociation is the cause of the blue sensation. In the cones which contain no visual purple, that substance does in reality exist, but is concealed by the presence of a second visual substance which is successively green, red and white in color (*i. e.*, is always complementary in objective color to the visual purple in all its color changes) and which is the source of our sensations of red and green. There is a third colorless substance in rods and cones alike whose decomposition is the source of the normal white-gray sensations, and of the sensations of the totally color-blind as well as of those of the normal eye when temporarily color-blind owing to insufficient illumination, besides contributing to the brightness of all sensations of light."

1894. Oliver J. Lodge. "The Work of Hertz." Nature, Vol. 50, p. 137.

In this review of Hertz's work a brief outline of an electrical theory of vision is given as follows: "I therefore wish to guess that some part of the retina is an electrical organ, say like that of some fishes, maintaining an electromotive force which is prevented from stimulating the nerves solely by an intervening layer of badly conducting material, or of conducting material with gaps in it; but that when light falls upon the retina these gaps become more or less

conducting and the nerves are stimulated. This intervening layer acts as a coherer affected by Hertzian waves, or as selenium affected by ordinary light. The sensation of light is due to electrical stimulus; the sensation of black is due to the mechanical or tapping-back stimulus. Vision is persistent until this latter stimulus occurs. The energy of vision is supplied by the organism, the light only pulls a trigger."

1894. A. König. "Ueber den menschlichen Sehpurpur und seine Bedeutung für das Sehen." Sitz. Akad. Wiss. Berlin, Vol. II., p. 577.

In his papers König has developed the Young-Helmholtz theory along the line of assigning specific functions to the rods, cones, and visual purple. "He believes that the cones have nothing to do directly with the luminous sensation, but that they are catoptric instruments for the purpose of condensing light upon the walls of the pigment epithelium, where the photochemical processes take place which are the sources of the sensations of red, yellow and green. The blue sensation is furnished exclusively by the visual yellow of the rods, and the sensation of a faint light (and that of the totally color-blind) is also blue in quality and is due to the visual purple. Hence the fovea, where there is no visual purple, is blind to blue. The blue blindness of the fovea has not been confirmed by other observers."

1895. W. Nicati. "Théorie de la coleur." Archiv d'Ophthal., XI., p. 1. Reviewed by C. L. Franklin, Psychol. Rev., Vol. 3, 1896.

The author uses such words as protochroism, metachroism, pleochroism, for gray vision, partial color-blindness and normal vision respectively. There is no difference in rods and cones that will cause three-color sensations, but in the "bipolar cells" there is a separation of the terminations into three layers for the three sensations. The visual purple is chemically affected by light and generates electric currents which are conducted by threads of varying resistances. The strength of current which is conveyed by each thread determines the character of the color sensation. Suitable cells are provided near the threads which send down condenser

discharges to undo the effects of the first currents. For example, after red has been seen the discharge causes green.

1896. G. E. Müller. "Der psychophysischen Axiome und ihre Anwendung auf die Gesichtsempfindungen." Zeit. für Psychol. u. Physiol. des Sinnes., Bd. 10, 1896, p. 1. Second paper; *ibid.*, p. 321. Also two other papers, Bd. 14, 1897. Reviewed by C. L. Franklin: "Professor Müller's Theory of the Light Sense." Psychol. Rev., Vol. 6, 1899, p. 70.

The theory set forth in these lengthy papers is a modification of Hering's. Instead of the dissimilation and assimilation of visual substances as provided by Hering, Müller takes advantage of a conception of modern chemistry, namely the reversibility of chemical action under suitable conditions, which conditions, he assumes, are realized in the retinæ of vertebrate animals. The chemical law of mass action is also used in treating of the intensity of the photochemical processes. The pairs of sensations are the same as in Hering's theory except that a slight difference is made in the white-black process. Müller makes use of the "self light" of the retina in modifying the antagonism which exists between the black and white sensations. These do not naturally counteract each other perfectly, and so Müller assumes that the "self light" produces the gray effects. No use is made of the visual purple as a substance for producing vision, but it is regarded as an aid in bringing about adaptation to faint light.

1897. J. von Kries. "Ueber Farbensysteme." Zeitschrift f. Psych., XIII., p. 241. "Krit. Bemerk. zur Farbentheorie," *ibid.*, XIX., p. 175. 1898.

Von Kries in what has been termed a "reconstruction" of the Young-Helmholtz theory apparently inclines to the view "that there are two sorts of white — one physiological and brought about by a photochemical dissociation in the rods; the other psychical and due to a mental reconstitution of an even red-green-blue sensation into a sensation of indistinguishable quality from the first." In the latter case the red, green and blue sensations are occasioned by disturbances of the cones alone.

1897. W. Patten. "A Basis for a Theory of Color Vision." Amer. Naturalist, 32, p. 833. Abstract: Science, N. S., 7, 1898, p. 219.

"The theory is based on the structure of retinal cells in invertebrates. The structures in the eyes of invertebrates corresponding to the rods and cones of vertebrates are generally composed of groups of simple or compound wedges, containing systems of transverse fibrils accurately graded in length, according to their positions in the wedges. The fibrils are always arranged in planes at right angles to the rays of light. All the fibrils in these planes may be parallel to one another, or at varying angles, or they may radiate from the axis of each rod like the bristles on a test-tube cleaner, so that no two fibrils in the same plane are parallel. By assuming that the length and angular relations of a fibril determine the amount of its response to a wave of light of a given length and plane of vibration, it is possible to offer a logical explanation of many phenomena of color vision."

1898. Adolph Stöhr. "Zur Hypothese der Sehstoffe und Grundfarben." Leipzig und Wien: Deuticke, 1898. Reviewed by C. L. Franklin: Psychol. Rev., Vol. 7, 1900, p. 415.

The author "assumes several visual substances, and also, in the end-apparatus of the optic nerve, ultra-microscopic visual elements or corpuscles which are excited, under proper conditions by the visual substances. It is further supposed that the direct action of light upon the visual corpuscles is already sufficient to set them into molecular vibration, and that the effect of the visual substance is simply to modify and to strengthen this vibration. The object of this duplex supposition is to combine in one a photo-chemical hypothesis and a photo-physical one. In the highest animals these substances are three in number, and they give rise to the elementary color sensations.

"The visual elements, corpuscles or threads as they are variously called consist of minute fibers each thickly strewn over its entire surface with projecting flat plates, four in a given plane, and composed of material of four different sorts fitted to respond to four different sorts of stimulus and to furnish three primary color sensations together with the sensation of white. The most characteristic part

of the theory is that these little plates are set into molecular vibration in the first instance by the direct action of light (all alike in this case, and attended by the white sensation), but in the second instance this vibration is added to by the synchronous molecular vibrations of the three photo-chemical substances, when severally produced by light of different periodicity. It is then neither the production nor the destruction of a photo-chemical substance that is effective in exciting the nerve terminals, but it is during its relatively brief period of existence that a given substance acts upon the particular color-plate with which it is in harmony."

The various theories outlined in this paper are shown in their mutual relationship to some extent in the accompanying figure. From Newton to Hering the development of color theory proceeded along one main line, the latter originating a new branch which rivals, and, in the opinion of many, completely overshadows the parent stem. By a combination of characteristic features of both Young-Helmholtz and Hering theories, Donders directed development along a third line. At present therefore color theorists are divided into three groups, the physicists conservatively holding to the main line, the psychologists and physiologists, while divided in their allegiance, for the most part accepting the hypothesis of Hering.

The chief theories are criticised from the psychological standpoint in the "Dictionary of Philosophy and Psychology" art. 'Color Vision.' Several are also treated at considerable length in Sir Michael Foster's "Text Book of Physiology," and in Calkins' "Introduction to Psychology," as well as in other works of a similar character. To these and to the critical reviews by Mrs. Franklin which are referred to in their place, as well as to Dr. J. W. Baird of the Department of Psychology, Cornell University, I am indebted for valuable information.

PHYSICS DEPARTMENT, CORNELL UNIVERSITY.

ON THE ASYMMETRY OF A MERCURY BREAK.

By James Edmund Ives.

IN a paper, now in the course of publication, in the *Philosophical Magazine*, I have described a peculiar property of a mercury break. While making some experiments to determine the law governing the capacity of the shunted condenser necessary to stop the sparking at the break of an inductive circuit, I discovered that it depends upon the direction in which the current is flowing through the break. The arrangement of the experiment is shown diagrammatically in Fig. 1, where *p* is a solenoid; *e*, a battery of one or more storage cells; *b*, a mercury break, and *c*, a shunted condenser. It will be noticed that the circuit consists of three branches: *opeo'*, containing the solenoid and the battery; *obo'*, containing the break, and *oco'*, containing the condenser. The break, itself, was an amalgamated copper wire, a millimeter in diameter, dipped by hand in and out of a small test-tube containing mercury. The test-tube was about two centimeters in diameter, and the mercury was covered with water to a depth of two or three centimeters. The least amount of capacity which must be inserted in shunt around the break to reduce the spark from a large to a small one, has been called, when the solenoid is the primary of an induction coil, the *optimum capacity*, and will be referred to by this name.

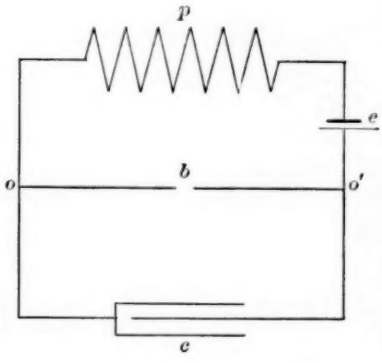


Fig. 1.

This dependence of the *optimum capacity* on the direction of the current is such a remarkable fact that I have undertaken some

further experiments to confirm it, and if possible to determine the cause of it. In the paper referred to, only one experiment dealing with this property of a mercury break is described, and the constants of the branched circuit are not given. Eight new experiments have been made and the results of three of these, typical of all, are given in Table I.

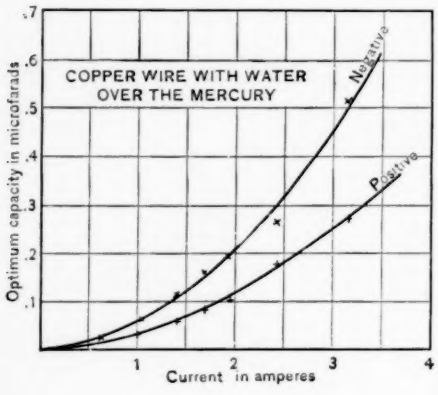


Fig. 2.

The relation between the optimum capacity and the current, when the breaking pole is an amalgamated copper wire and the mercury is covered with water, is shown by the curves of Fig. 2, plotted from the results of Experiment 1, Table I. In these curves the asymmetrical behavior of the current is shown very clearly, the optimum capacity being much greater when the breaking pole is

TABLE I.

Experiment 1. Amalgamated Copper Wire. Water over the Mercury.			Experiment 2. Amalgamated Copper Wire. No Water over the Mercury.			Experiment 3. Iron Wire. No Water over the Mercury.		
Current in Amperes.	Optimum Capacity in Microfarads.		Current in Amperes.	Optimum Capacity in Microfarads.		Current in Amperes.	Optimum Capacity in Microfarads.	
	Breaking Pole Positive.	Breaking Pole Negative.		Breaking Pole Positive.	Breaking Pole Negative.		Breaking Pole Positive.	Breaking Pole Negative.
.63	.018		.80	.038	.060	.70	.018	.038
.55		.020	1.00	.060	.092	.87	.024	.047
1.03	.033	.065	1.39	.105	.165	1.08	.035	.082
1.40	.060	.119	1.73	.155	.250	1.53	.070	.159
1.69	.084	.159	1.95	.195	.326	1.90	.117	.246
1.94	.104	.194	2.36	.261	.456	2.15	.134	.261
2.42	.177	.265	3.13	.412	.801			
3.15	.274	.515						

negative than when it is positive. By the breaking pole "negative" is meant that it is connected to the negative side of the battery e. When "positive" it is connected to the positive side of the battery.

The change in the direction of the current through the break was made by commuting the connections to the battery. In all these experiments the electromotive force of the battery, consisting of two storage cells, was 4.2 volts; the resistances of the branches *obo'* and *oco'* were each .1 of an ohm. The inductance of the solenoid, used in all the experiments without an iron core, was .000281 of a henry. The current was varied by inserting non-inductive resistance in the branch *opeo'*. The only inductive resistance in the branched circuit was that of the solenoid.

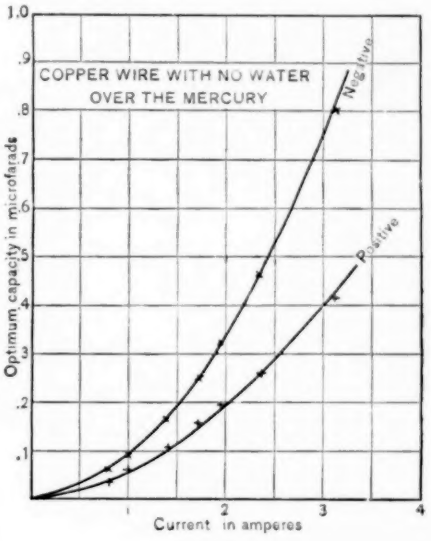


Fig. 3.

Thinking that this asymmetry might depend in some way upon the layer of water over the mercury, I made an experiment without any water above it, and obtained the results shown in Experiment 2, Table I., and in Fig. 3.

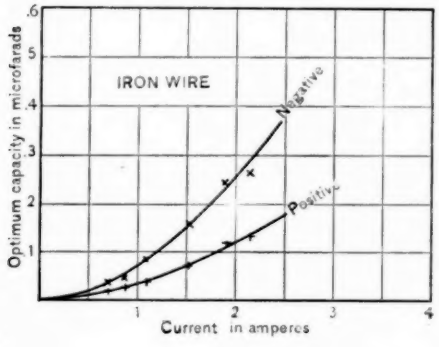


Fig. 4.

It will be seen that the curves are essentially similar to those of Fig. 2. It then seemed that it might be due in some way to the amalgam in the copper wire, and an iron wire .87 of a millimeter in diameter was used instead. The results are given in Experiment 3 Table I. and in Fig. 4. The curves are similar to those of Fig. 2and Fig. 3. Since iron does not amalgamate under any circumstances, the effect is not due to the copper amalgam. In the same way a platinum wire was tried, and curves obtained similar to those of Fig. 4.

My first hypothesis was, that it was due to the fact that in the ordinary mercury break we have a spark passing between a point and a plane, the end of the wire being the point, and the surface of the mercury the plane. To test this, the break was made between an iron wire and a thread of mercury in a capillary tube. The diameter of the iron wire was .07 of a millimeter, and the diameter of the tube about a millimeter. The results obtained were similar to those of Fig. 4. Since, in this case, the break occurs between two points, and not between a point and a plane the effect is not due to this cause.

In seeking for an explanation it must be remembered that when the circuit *opeo'bo* is broken at *b*, an oscillatory current is set up in the circuit *opeo'co*. It seems possible that the asymmetry may be due to some selective action of the mercury vapor generated when the spark passes, of the same nature as the recently discovered Cooper-Hewitt effect. Or it may possibly be due to some capacity effect, such as is found in the Wehnelt interrupter.

I take pleasure in acknowledging the assistance rendered me in these experiments by Mr. Gordon Farnham, of the University of Cincinnati.

PHYSICAL LABORATORY, UNIVERSITY OF CINCINNATI,
March, 1903.

DO FALLING BODIES MOVE SOUTH?

By Edwin H. Hall.

Part I., Historical.

THE question whether a sphere falling from rest through a few hundred feet of still air swerves perceptibly toward the south, from the vertical path indicated by the plumb-line, is not, perhaps, one of the largest or most urgent problems of physics; but it has the dignity of venerable age and the charm of mystery. It was familiar to Newton; it has been answered in the negative, on theoretical grounds, by Gauss and by Laplace, and in the positive, on experimental grounds, by nearly every one of the investigators who have from time to time through more than two centuries made the actual trial.

If there is any significant feature of this problem, in its purely mechanical aspects, which Gauss and Laplace failed to perceive or could not adequately discuss, the discovery of this feature and its function is a worthy task for any mathematician of the present day. If there is any explanation in electric or magnetic action for a southerly deviation of perceptible magnitude, under the conditions of experiment which have prevailed, this explanation is yet to be offered by any physicist, though several have made the attempt. If the well-nigh universal agreement of experimental evidence as to the reality of such an effect is the result of a long succession of accidental errors in one direction, we have a striking exception to the ordinary course of chance events. If the whole mystery is the consequence of mental bias in the experimenters, the proof and explanation of this bias would have, at least, the merit of psychological interest.

Accordingly, it seems worth while to go over carefully all that is known in regard to the experiments in question, with a view to estimating, not merely the degree of skill and care shown in each, but also the mental attitude of each experimenter with regard to

the issue of his work. In *Science* for November 29, 1901, Professor Cajori published an admirable summary of the history of our problem, describing briefly the results of all notable investigations upon it, whether experimental or theoretical. But for our purpose there is need of details which Professor Cajori did not give. Much of what immediately follows in regard to English investigators is taken from Mr. W. W. R. Ball's *Essay on Newton's Principia.*

In November, 1679, Robert Hooke wrote to Isaac Newton proposing a philosophical correspondence. The latter replied, declaring that he had "shook hands with philosophy," had "long grutched the time spent in that study," and was now busy with other affairs, but proposing a scrutiny of the course of falling bodies as a means of demonstrating the revolution of the earth. "Let *A* be a heavy body suspended in the air, and moving round with the earth so as perpetually to hang over the same point thereof *B*. Then imagine this body . . . let fall, and its gravity will give it a new motion toward the center of the earth without diminishing the old one from west to east. Whence the motion of this body from west to east, by reason that before it fell it was more distant from the center of the earth than the parts of the earth at which it arrives in its fall, will be greater than the motion from west to east of the parts of the earth at which the body arrives in its fall; and therefore it will not descend the perpendicular . . ., but outrunning the parts of the earth will shoot forward to the east side of the perpendicular, describing in its fall a spiral line . . ., quite contrary to the opinion of the vulgar who think that, if the earth moved, heavy bodies in falling would be outrun by its parts and fall on the west side of the perpendicular." Newton added some very interesting suggestions as to the method of trying such an experiment. He would use a pistol bullet, on a calm day, would have the bob of the plumb-line "setled in water so as to cease from swinging," and would by preference work in "a high church or wide steeple, the windows being first well stopped; for in a narrow well the bullet possibly may be apt to receive a ply [push?] from the straightened [compressed?] air neare the sides of the well, if in its fall it come nearer to one side than to another."

On December 4 of the same year, Hooke laid Newton's pro-

posal before the Royal Society, and an interesting discussion followed, in the course of which "Sir Christopher Wren supposed, that there might be something of this kind tried by shooting a bullet upward at a certain angle from the perpendicular round every way, thereby to see whether the bullets so shot would all fall in a perfect circle round the place where the barrell was placed."

On December 11 Hooke read to the society his answer to Newton's letter, maintaining that the course of the falling body "would not be a spiral[1] line, as Mr. Newton seemed to suppose," and "that the fall of the heavy body would not be directly east, as Mr. Newton supposed; but to the southeast, and more to the south than the east."

January 6, 1680, Hooke wrote to Newton: "In the meantime I must acquaint you that I have (with as much care as I could) made three tryalls of the experiment of the falling body, in every one of which the ball fell towards the southeast of the perpendicular, and that very considerably, the least being above a quarter of an inch, but because they were not all the same I know not which was true. What the reason of the variation was I know not, whether the unequal spherical figure of the iron ball, or the motion of the air, for they were made without doors, or the insensible vibration of the ball suspended by the thread before it was cut."

A little later Hooke answered Newton that "by two tryalls since made in two severall places within doors it [the same experiment] succeeded also," and on January 22, 1680, before the Royal Society, "Mr. Hooke showed the ball, that had been let fall from the hight of 27 feet, and fell into a box full of tobacco pipe-clay, sticking in the clay, upon the surface of which were made lines crossing each other: which showed the true perpendicular point indicated by the ball, when it hung suspended by a thread from the top, and how much the ball had varied from that perpendicular in its descent towards the South and East: and he explained the manner, how the same was performed in all particulars. It was desired, that this experiment might be made before a number of the Society, who

[1] This criticism stimulated Newton to a renewed study of the general law of gravitation, which he had not yet demonstrated, and years afterward became one of the chief points of discussion in the controversy as to how much assistance Newton had received from Hooke in the discovery or development of this law.

might be witnesses of it before the next meeting. The time appointed was the Monday following at three in the afternoon." This apparently ends the account of Hooke's observations. He was Secretary of the Royal Society; and if his experiment had been successfully repeated before the witnesses proposed, it is altogether probable that he would have recorded the fact in some public form.

In what has been quoted Hooke is entirely positive and somewhat circumstantial. Why is he not conclusive? Partly because his trials of the fall were so few, apparently only five in all, partly because the deviations which he recorded were so large in proportion to the very moderate height which he appears to have used. Moreover, Hooke, a brilliant genius but a somewhat uncertain character, had committed himself in the most open way to the opinion that experiment would reveal a southerly deviation. In a man of his reputation such a bias is not to be overlooked; and yet it is hard to believe that he deliberately lied to his associates of the Royal Society. His evidence is not to be altogether ignored.

Left in this dubious state by Hooke, our problem appears to have remained untouched for more than a century, until, in 1791, Guglielmini at Bologna took it in hand. He published a book in regard to the matter, but this book, if it exists still, is extremely rare, and few details of his work are now generally available. It was doubtless better than that of Hooke. He used a much greater fall, about 78 m., and appears to have made as many as sixteen trials. From these he deduced an average easterly deviation of about 1.9 cm. and an average southerly deviation of about 1.2 cm. He had a theory, whether formed before or after his experimenting the writer does not know, which attributed the southerly deviation to the resistance of the air. Indeed, his theory called for a somewhat smaller easterly deviation and a somewhat larger southerly deviation than his experiments produced.

But here, too, there were doubts. According to Benzenberg,[1] writing some twelve years later, "Guglielmini's experiments were made with great accuracy, but he first verified his perpendicular line six months after the experiments." In a footnote Benzenberg

[1] Gilbert's Annalen der Physik, Vol. XII.

quotes Lalande as follows: "Guglielmini writes me that he is now convinced that Laplace is right, and that the theory gives no deviation toward the south. That which he has found toward the east agrees very well with the theory; but this is now no longer proof of the motion of the earth, since the other deflection, toward the south, does not at all agree."

In 1802 Benzenberg was much occupied with falling balls in the tower of St. Michael's at Hamburg. Most of his experiments were on the resistance offered by the air to such bodies, this resistance being deduced from the length of time occupied in a given fall as compared with the time which would have been required in a vacuum. He measured the duration of the fall by means of a watch at the top of the tower, and the paucity of experimental resources in those ante-electrical days is strikingly shown by the fact that he could not get this time for a height greater than a certain number of feet, perhaps 250, because, beyond this limit, he could not at the top of the tower hear the thud of the ball when it struck on a block of wood at the bottom. After these experiments on resistance he made, during the same year and in the same place, observations on the easterly and southerly deviations. For this purpose he dropped 32 balls, finding an average easterly movement of 0.90 cm. and a corresponding southerly movement of 0.34 cm. Was Benzenberg in undertaking this research prepossessed in favor of a southerly deviation? Possibly, for he knew of the work of Hooke and of Guglielmini, and he had not yet received from Gauss those letters which finally convinced him of the improbability of such a phenomenon. That he took the evidence of his own experiments seriously is shown by the fact that he did not at once yield to the authority of Gauss, but questioned whether some feature of the theory had not been overlooked. Later he appears to have received without opposition the suggestion, from Olbers, that air currents had affected the course of the balls dropped in the Hamburg tower. So far as the writer knows, this suggestion was entirely without proof.

Discussion of our problem was at its height just a century ago. Gauss in 1803 and Laplace about the same time, each in his own

way, developed the theory of a sphere falling from rest through still air under the influence of gravity alone, that is, without effect from magnetic, electric, or other obscure forces. Each pronounced the southerly deviation inappreciable, for experimental heights. It is not unlikely, therefore, that Benzenberg, when in 1804 he resumed his experiments on falling bodies, was affected by a strong prepossession against the existence of a perceptible southerly movement.

He worked now in the vertical shaft of a coal mine at Schlebusch, with a fall of 84.4 m. His preparations and arrangements were made with care and intelligence. To prevent air currents he covered the top of the shaft and stuffed the passage at the bottom with straw. He suspended each ball before its release by means of a horse hair gripped between the jaws of a vise, and, lest there should be a disturbing bulge in the hair just above the part flattened by the vise, he flattened the hair in advance by drawing it between two hot irons. "The sphere hangs by a flattened horse-hair in a closed space and beneath is an opening through which it falls at release. Together two crossed microscopes are brought to bear, in whose common focus the horse-hair plays. . . . It takes always more than an hour, before a sphere comes quite to rest." "When the sphere is absolutely still, a light pressure opens the finely polished jaws of the vise, and the sphere falls." "Below lies a plank of wood [*Packholz*], which has in the middle a small hole through which the plumb-line of the point of suspension of the ball goes." Across the middle of the hole ran two threads, one of which marked the meridian, the other the parallel of latitude of the place. The ball made a sharply defined dent in the wood, and the distance of the middle point of this impression from both the meridian and the parallel was taken. Benzenberg remarks at one point that he has provided forty spheres for the research, and as these were probably made, like those he had previously used, of an alloy of the softer metals, it is unlikely that he could use any one of them more than once; so that, presumably, he made not more than forty trials in this later work.

Details of the observations at Schlebusch the writer has never seen. Benzenberg stated his conclusion briefly thus: "In still,

uniformly heated, air no such [southerly] deviation takes place, and the balls swerve only toward the east from the perpendicular." Cajori, who has apparently found some fuller account of this work than has come under the eye of the writer, says that "on selecting from the total number those experiments which, in his [Benzenberg's] judgment, were made under the most favorable conditions, there seemed to be no indication of a S. D."

The honesty of Benzenberg is not to be questioned. But we may well ask how far he may have been influenced, in "selecting" his evidence from the whole body of data, by the knowledge that the authority of Gauss and of Laplace was dead against the southerly deviation.

Whatever answer we may find for this question, the general belief among scientific men after 1804 must have been in accord with the opinion of the mathematicians, confirmed as it seemed to be by the work of Benzenberg. Accordingly, when Reich, in 1831, took up the problem which had been left undisturbed for nearly a generation, he can hardly, from previous evidence, have expected to find a deviation toward the south. He too worked carefully, profiting by the experience of his predecessors and making some changes of method which were possibly improvements. For example, he dropped his spheres, an alloy of tin, bismuth and lead, through a wooden spout erected especially for the purpose. The idea was good, as such a spout would prevent general horizontal draughts of air; but as we are told nothing about the size of the spout or the care taken to have the line of fall coincide with its axis, one may well be in doubt whether Newton's "ply from the straitened air neare the sides" was not in action here. Reich used sometimes the same method of release that Benzenberg had described and sometimes a curious method of his own "by means of an exactly horizontally placed ring, which was of such size that the balls when hot did not fall through it but when cold did fall through." He heated the ball in hot water, dried it, placed it on the ring and left it to fall through in its own good time. The defence of this unpromising device is that it seems to have worked better, causing less individual variation in the course of the balls,

than the other. At the bottom of the fall Reich's arrangements were much like those of Benzenberg, already described. The height he used was 158.5 m., in the shaft of a mine at Freiburg. The following is a summary of his observations as at first recorded, though later the correction of an error in the direction of his meridian line reduced the mean southerly deviation about 0.07 cm.

Series.	No. of Balls.	S. D.	Probable Error.
1	22	+0.6686 cm.	0.992 cm.
2	12	+2.3050 "	1.654 "
3	12	−0.1358 "	1.572 "
4	18	+1.2492 "	1.524 "
5	21	−0.7881 "	0.606 "
6	21	−1.6017 "	1.413 "
	106	+0.5061 cm. [?]	0.27 cm.

Even with the correction for error of meridian Reich found a very considerable S. D., more than 0.4 cm. He had made a more extensive study of the problem, had dropped more balls, than any of his predecessors. Was the evidence he had found conclusive? No. If we were to omit his series 2, the one having the smallest number of balls and the largest probable error, we should have from the other five series not a southerly, but a northerly, deviation. The margin is too narrow.

Oersted, writing to Sir John Herschel a letter which was printed in the B. A. Report for 1846, makes interesting comments on the work of Guglielmini, Benzenberg, and Reich. He regards the work of the last as the best, but says that Reich's observations "differed much among themselves, though not so much as those of Dr. Benzenberg." He concludes: "After all this there can be no doubt that our knowledge of this subject is imperfect, and that new experiments are to be desired." He urges English men of science especially to this research, because of the superior facilities and resources for such work in England.

The only practical result of this appeal known to the writer was the experiment made by Rundell, who dropped balls and various other objects about 400 m. down the shaft of a mine in Cornwall. Rundell appears to have had no knowledge of the details of the

devices used by his predecessors, and his own methods were crude, as the following account of them, given by himself in the *Mechanic's Magazine*, Vol. 48, 1848, will show:

"A strong rectangular frame was constructed, having a shelf or stage inside it, capable of turning freely upon an axis, supported by pointed centers, fixed in the sides of the frame. This frame was placed in a horizontal position over the shaft; and when the moment arrived for dropping the bullet, its support was suddenly removed by turning the stage round its axis.

"This plan, it is conceived, ensures the dropping of the bullet, without an appreciable tendency to any particular direction arising from the method employed. It may, perhaps, be objected that the cohesion between the shelf and the bullet would impart to the latter a motion in the direction in which the shelf moved. This is the case when the shelf is made to move very slowly, but when it is turned suddenly on its axis, even if it be some degrees from the truly horizontal position, no deviation arises from this source, as was clearly proved by preceding and subsequent experiments [not described].

"Besides the bullets, iron and steel plummets were used, the latter being magnetised. In form these were truncated cones, the lower and larger ends being rounded. These were suspended by short threads inside a cylinder, to prevent draughts of air affecting them, and when they appeared free from oscillation, the threads were let go. The number of bullets used was forty-eight and there were some of each of the following metals, iron, copper, lead, tin, zinc, antimony, and bismuth.

"A plumb-line was suspended at each end of the frame and east and west of each other; to these were attached heavy plummets, the lower ends pointed. After they had been hanging for some hours in the shaft, a line joining their points was taken as a datum line from which to measure the deflection.

"The whole of the bullets and plummets dropped south of this datum line, and so much to the south that only four of the bullets fell upon the platform placed to receive them, the others, with the plummets, falling on the steps of the man-machine, on the south side of the shaft, in situations which precluded exact measurements of the distances being taken. The bullets which fell on the platform were from 10 to 20 ins., south of the plumb-line.

"The deflection being much greater than I had anticipated could arise from any cause which appeared likely to produce a deviation, I feared the whole experiment was a failure, but more recent considerations have induced me to again test the method employed, [and] I feel confident that the deflection is not due to errors arising from the method of dropping the bullets, and that it is not at all likely that draughts of air in the shaft had any important influence on the result, but that there is a real deflection to the *south of the plumb line*, and that in a fall of a quarter of mile it is of no small amount."

A deviation of ten or twenty inches at the least, and nobody knows how much more, is large enough to be interesting. Unfortunately it is, as Rundell himself felt, hardly credible. Some grave fault of method or conditions is probable here. The manner of release of the bullets, by suddenly tipping the shelf on which they have been resting, is open to criticism, in spite of the confidence which he expresses in it. Indeed, this rather naïve confidence is the opposite of reassuring, as it seems likely that the sudden movement of the shelf would cause a disturbing current of air, if not some more direct mechanical action affecting the course of the bullets; and Rundell describes no experiments to justify his method in this particular. The fact, however, that the "plummets," which were released in a radically different way, all went far to the south, makes it probable, though not certain, that the main cause of the universal southerly movement in these experiments is not to be found in the method of release. The possibility of disturbing draughts of air is disposed of much too lightly by Rundell.

Moreover, we are told too little about the plumb lines, a criticism which applies to all the researches which have been reviewed in this paper. The lower end of a steel or iron wire would be deflected more or less, according to the weight of the plummet supported by it, from the vertical toward the north. Benzenberg probably used a silver wire; Reich used a copper wire. We are not told what kind of wire Rundell used, or Guglielmini, or Hooke.

Curious things may well occur when a plumb-line is suspended or a ball let drop in deep mine shafts not especially prepared for the experiment. Recent observations in the Tamarack, with a depth of more than 4,000 feet, showed two steel wires, carrying each a fifty-pound weight, to be farther apart at the bottom than at the top.

Balls let fall in the same shaft, which is many feet wide, have, the writer is informed, apparently failed to reach the bottom, lodging somewhere on the way down. Air currents are now believed to explain the divergence of the plumb-lines, and air currents possibly may be responsible for the fate of the balls. The fact that a plumb-line in the shaft of an important mine may be at fault gives to our problem a suggestion of utilitarian interest.

In 1902 the writer made, in the inclosed tower of the Jefferson Physical Laboratory of Harvard University, by far the most elaborate and extensive research of which we have record on the course of falling spheres. Details of the method used will be given in another paper. The distance available was small, about 23 m., but the convenience of working in a well-equipped laboratory made possible a very large number of trials. After dropping some hundreds of balls in preliminary practice and development of details of procedure, the writer dropped 948 balls and took the mean deviations, to the east and to the south, for these cases. The result was, for the southerly deviation, 0.005 cm., about the five-hundredth part of an inch, with a "probable error" not much smaller.

If this result stood alone, it might well be considered as practically negative, discouraging belief in a southerly deviation. If the work of any other investigator in this field stood alone, it might well be disregarded, as raising no sufficient presumption in favor of the effect looked for to warrant the undertaking of further experiments. But the well-nigh invariable occurrence of an apparent movement toward the south,[1] the only exception being in the second research of Benzenberg, is a fact not properly accounted for by the history of our problem. Granting that Hooke was prejudiced and may even have merely pretended to find a southerly movement,

Observer.	Time.	Place.	Fall.	S. D.	E. D.	S. D. + E. D.
Hooke.	1680	London.	8.2 m.	+	+	?
Guglielmini.	1791	Bologna.	78.3	1.19 cm.	1.89 cm.	0.63
Benzenberg.	1802	Hamburg.	76.3	0.34	0.90	0.38
"	1804	Schlebusch.	84.4	0.	+	0.
Reich.	1831	Freiburg.	158.5	0.44	2.84	0.16
Rundell.	1848	Cornwall.	400.	25–50	?	?
Hall.	1902	Cambridge.	23.	0.005	0.149	0.03

[1] A summary of results is here given, S. D. standing for southerly deviation, and E. D. for easterly deviation :

granting that every experimenter probably wanted to find some deviation, a positive result in such a research being far more interesting than a negative one, granting that in a case like this, which presents great difficulties and uncertainties, a prejudice in favor of this or that result may lead the experimenter to look farther, so long as his expectation is not fulfilled, and to stop when his expectation is fulfilled—granting all this, the writer finds himself unable to remain quite content with the theory that these conditions have created out of nothing the general evidence in favor of a southerly deviation. Further investigation, under the best possible conditions, appears to the writer worth while, if only to establish a satisfactory negative, so that the question before us may vex no mortal more.

Where can these best possible conditions be found? Apparently in the great monument[1] at Washington. For something like a sheer five hundred feet this great pile has neither window nor crevice opening to the outer air. It can, therefore, be almost hermetically sealed against interior disturbance from winds. There is between the stairway and the elevator, on both the north and the south side, a clear space some thirty inches wide all the way from the "deck" at the top to the base.

But is not the top of so tall and slender a shaft all the time in a state of quiver which would give to the balls a lateral motion before their release, and thus cause them to wander widely in their long descent? Apparently not, at least when there is no wind. During a visit last January to the monument, the writer was surprised to find a mercury surface at the top much less disturbed than it commonly would be in the Physical Laboratory at Cambridge. The mud of the Potomac flats, in which the unfinished shaft once threatened to sink, has at least the merit of being an admirable insulator from the jar of traffic in the nearest streets, which, indeed, are a good distance away. No doubt, in a high wind the top of the monument would quiver, and dropping balls in it in such a case, would be worse than labor wasted, for our present purpose. But, given a year, one might undertake there a research which should be conclusive, yielding a final answer to the question which stands at the head of this paper, a question which has been asked so many times in vain.

CAMBRIDGE, MASS.

[1] Cajori has suggested this place.

NEW BOOKS.

Vorlesungen über theoretische Physik. Von H. von HELMHOLTZ. Band VI., Vorlesungen über Theorie der Wärme, herausgegeben von Franz Richarz. Pp. xii + 419. Barth, Leipzig, 1903.

The readers of the sixth volume of Helmholtz's "Theoretical Physics" are fortunate in having as editor of this, which is in some respects the most important portion of the great work of the master, one who had the opportunity of obtaining, at first hand, notes from Helmholtz's lectures as they were delivered to his classes in Berlin and who appreciated the importance of preserving so far as possible the form and personal idiosyncrasy of the original. Professor Richarz has performed this delicate and difficult task in a manner for which all those who have ever had the privilege of listening to the lectures of Helmholtz will be thankful. To such readers the volume will be found to have an especial charm. On nearly every page the personality of the author makes itself felt. This rare quality would inevitably have been lost had an attempt been made to supplement the original with new material. The highest value of such a book does not consist in striving for completeness or by bringing it up to date by the insertion of new matter, but in enabling us to see the subject as Helmholtz saw it and as he presented it in his lectures to his classes.

The task of presenting to the scientific public in a connected and consistent form the wealth of material which Helmholtz offered to his hearers throughout a long period was by no means a simple one. The presentation of the subject in the lecture room was not the same from year to year. His lectures also had a certain impromptu element, which while it did not detract from the interest or value of them, distinguished them, for example, from the perfectly systematized and fully developed courses given in theoretical physics in Berlin by Kirchhoff. Helmholtz was in the habit of taking up the subject, as it were anew, upon each occasion and of attacking his problem from whatever standpoint appealed to him at the moment. Professor Richarz is fortunate enough to have in addition to the stenographic report of the lectures as given in the winter of 1892–1893, prepared at the special request of his pupils at that time by Dr. Borchordt, and in great part corrected by the author before his death, Helmholtz's original note-books and his own set of notes taken in 1882–1883. By the judicious use of these materials he has succeeded in

incorporating in the present volume a fuller and more comprehensive treatment of the subject than was given in any single year without introducing any element of discontinuity or lack of sequence. The volume includes as its chief subjects the conductivity of heat, the mechanical theory of heat, in the establishment of which the author had had in earlier years so important a part and the kinetic theory of gases, to the development of which he had likewise been one of the principal contributors. E. L. N.

A Treatise on the Theory of Solution Including the Phenomena of Electrolysis. By W. C. D. WHETHAM. Pp. 475. The University Press, Cambridge, 1902.

This volume is an outgrowth of the smaller book "Solution and Electrolysis," published in 1895. There is a preliminary chapter on thermodynamic principles; then follow chapters on the application of the phase rule to one-component and two-component systems. General solubility relations are next considered and then comes a discussion of osmotic pressure. The author is then in a position to discuss quantitative relations between concentration and change of vapor pressure. The results are summoned up in a chapter on theories of solution. This is an orderly and logical development of the subject.

Having established the general facts in regard to solutions, the author considers electrolysis, conductivity of electrolytes, galvanic (better voltaic) cells, contact electricity and polarization. After this comes the theory of electrolytic dissociation, diffusion in solutions and solutions of colloids.

This is a very interesting book and shows a general sanity of treatment which we do not always find in books of this sort. On p. 128 the juggling with the molecular weight of the liquid is unfortunate and misleading. The table of electro-chemical properties of aqueous solutions printed as an appendix is admittedly ten years old.

WILDER D. BANCROFT.

Niels Henrik Abel, Memorial Publie a L'Occasion du Centenaire de sa Naissance, Kristiania. By JACOB DYBWAD. 1902. (Received.)

Die Theorie der Collectivgegenstande. By GOTTL. FRIEDR. LIPPS. Pp. i + 215. Leipzig. Verlag von Wilhelm Engelmann, 1902. (Received.)